FEB 27 '45

UNITED STATES DEPARTMENT OF COMMERCE

Journal of Research

of the

National Bureau of Standards

Vol. 33, No. 6 December 1944

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Journal of Research

of the

National Bureau of Standards

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Volume 33, Number 6
December 1944

[Published with approval of the Director of the Budget]

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1945

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1618

Part of *Journal of Research of the National Bureau of Standards, Volume 33, December 1944*

STANDARD RESPONSE FUNCTIONS FOR PROTANOPIC AND DEUTERANOPIC VISION

By Deane B. Judd

ABSTRACT

The color matches set up by the normal observer can be predicted satisfactorily by three functions of wavelength defining the ICI standard observer. It has been found possible by a transformation of coordinate system to express these three functions in a form such that two of the three pairs also represent the color matches of the two recognized types of red-green-blind observer, the protanope and the deuteranope, within the rather small uncertainties to which they are known. The remaining pair of functions represents, within the comparatively large uncertainties to which they are known, the color matches of the tritanope, a more rare type of observer who confuses reddish blue with greenish yellow. These three functions, therefore, serve to relate the color matches made by dichromats to those made by normal trichromats, and so make conveniently accessible the color confusions of average dichromatic observers. The use of these three functions in the solution of problems arising in the design of tests for colorblindness is illustrated by solution of three such problems, and their connection to theories of color vision is discussed.

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I. INTRODUCTION

When the two halves of a photometric field are illuminated to the same degree with light of the same spectral composition, they cannot be distinguished; that is, they produce a color match. But it is possible also to produce a color match between lights of different spectral compositions; such lights are called metamers [22, 51] [1] and

[1] Figures in brackets indicate the literature references at the end of this paper.

are said to form metameric pairs. The functions that give the conditions to be met by the spectral composition of any two lights in order that they shall form a metameric pair for a given observer serve to define the characteristics of that observer; and in 1931 the International Commission on Illumination adopted such functions, which define the standard observer [23, 27].

Protanopic and deuteranopic vision are the two most common forms of dichromatic vision, each form occurring in about one percent of otherwise normal human males [31]. They are known as reduction forms because neither a protanope nor a deuteranope ordinarily distinguishes the members of any pair of normal metamers; that is, a color match set up by a normal observer will not be objected to by a dichromat unless the pigmentation of his eye media, including the macula, be grossly different from that of the normal observer [38b]. The standard color specifications are therefore generally valid for dichromats in the sense that if two lights have the same standard color specifications, no average dichromat will be able to distinguish them.

These specifications are, however, unnecessarily complicated for such observers. In addition to normal metamers, dichromats find many other pairs that they cannot distinguish. These additional metamers are often called confusion colors; they are colors that are distinct to the normal although identical to the dichromat. The normal color specification consists of three numbers because the normal visual system is capable of three independent modes of variation and on that account is often called trichromatic. The dichromatic specification need consist of but two numbers. These two numbers may be derived from the standard color specification in a simple way. The connection between trichromatic and dichromatic specifications was indicated in complete detail by Maxwell in 1855 [44] by appeal to the Young theory of vision. The original simple form of this theory has been disproved, the extensions of it vary with the phenomena to be explained, and there is doubt whether the theory, however extended, can yield more than a partial explanation of the complicated facts of vision. However, the connection between dichromatic and trichromatic color specifications first worked out by Maxwell on theoretical ground does not depend upon the portions of Young's hypothesis now given up; on the contrary this connection has been repeatedly proven to be correct. It is the purpose of this paper to derive, by this principle, response functions for protanopic and deuteranopic vision, to show how they may be used to find whether or not two colors will be confused by an average protanope or average deuteranope, and finally to point out a few of the theoretical implications of the functions chosen.

II. THEORY

Maxwell wrote in his letter of January 4, 1855 to George Wilson [44]: "If we find two combinations of colours which appear identical to a Colour-Blind person, and mark their positions on the triangle of colours (now called the Maxwell triangle), then the straight line passing through these points will pass through all points corresponding to other colours, which, to such a person, appear identical with the first two.

"We may in the same way find other lines passing through the series of colours which appear alike to the Colour-Blind. All these lines either pass through one point or are parallel, according to the standard colours which we have assumed, ... Knowing this law of Colour-Blind vision, we may predict any number of equations which will be true for eyes having this defect.

"The mathematical expression of the difference between Colour-Blind and ordinary vision is that colour to the former is a function of two independent variables, but to an ordinary eye, of three; and that the relation of the two kinds of vision is not arbitrary, but indicates the absence of a determinate sensation, depending perhaps upon some undiscovered structure or organic arrangement, which forms one-third of the apparatus by which we receive sensations of colour."

The straight lines on the Maxwell triangle serve to indicate the chromaticity confusions of the colorblind observer. The point of intersection of these lines indicates the normal chromaticity of the primary process not possessed by the colorblind. Suppose for the protanope that the chromaticity-confusion lines are copunctal at (x_p, y_p) on the (x, y)-plane of the standard ICI colorimetric coordinate system [23, 27], and suppose for the deuteranope that the corresponding point is (x_d, y_d). Let us inquire how to derive from the functions (of wavelength) (X, Y, Z) defining the standard normal observer, three new functions (W_d, W_p, K) such that all three taken together represent the normal observer; such that (W_d, K) taken together represent average deuteranopic vision, and such that (W_p, K) taken together represent average protanopic vision. This terminology (W_d, W_p, K) is taken from v. Kries [39, p. 164] who followed König [37] closely. The symbol W is intended to suggest "warm"; and K, "cold" (*kalt*), corresponding to whatever warm color (orange, yellow, greenish yellow) and whatever cold color (blue or violet) is sensed by red-green-blind observers.

The derivation consists of making new choices of primary processes such that two of them correspond to (x_p, y_p) and (x_d, y_d), respectively. It was pointed out by König in 1886 [37] for this very purpose, and by many others since [13, 24, 25, 43, 54] for other purposes, that such choices result from defining the new functions (W_d, W_p, K) as weighted sums of the old, thus

$$\left.\begin{aligned} W_d &= k_1X+k_2Y+k_3Z \\ W_p &= k_4X+k_5Y+k_6Z \\ K &= k_7X+k_8Y+k_9Z \end{aligned}\right\}, \tag{1}$$

where k_1 to k_9 are constants that may be given any arbitrary values whose determinant differs from zero:

$$\begin{vmatrix} k_1, & k_2, & k_3 \\ k_4, & k_5, & k_6 \\ k_7, & k_8, & k_9 \end{vmatrix} \neq 0. \tag{1a}$$

Since the point (x_p, y_p) corresponds to the primary, W_d, not possessed by the protanope, $W_p=K=0$, for $X/(X+Y+Z)=x_p$, and $Y/(X+Y+Z)=y_p$, and we may write from eq 1:

$$\left.\begin{aligned} k_4x_p+k_5y_p+k_6z_p &= 0 \\ k_7x_p+k_8y_p+k_9z_p &= 0 \end{aligned}\right\}, \tag{2a}$$

where z is defined as $Z/(X+Y+Z)$ and is equal to $1-x-y$.

Similarly, since the point (x_d, y_d) corresponds to the primary not possessed by deuteranopes, we may write:

$$\left.\begin{aligned} k_1x_d+k_2y_d+k_3z_d=0 \\ k_7x_d+k_8y_d+k_9z_d=0 \end{aligned}\right\}. \tag{2b}$$

The four conditions expressed by eq 2a and 2b are the only conditions that have to be met to insure that W_p and W_d represent the primary color processes not possessed by the deuteranope and protanope, respectively. Since nine conditions are required to determine the nine constants of eq 1, it may be seen that many coordinate systems can serve both for normal trichromatic visual systems and for dichromatic systems by neglect of the one or the other of two of the three normal components.

Two of the remaining five degrees of freedom are required to insure, as is convenient, that the equal-energy stimulus be kept as the basic stimulus [14] of the system, that is, that it be represented at the center of the Maxwell triangle of the new coordinate system as well as in the standard ICI system. This requirement is satisfied if the distribution curves of the new primary color processes throughout the equal-energy spectrum be adjusted, like those of the ICI system, to equal areas; that is, if $k_1+k_2+k_3=k_4+k_5+k_6=k_7+k_8+k_9$. Another degree of freedom must be expended to set the arbitrary units in which the distribution curves are expressed. The three conditions together may be expressed conveniently as:

$$\left.\begin{aligned} k_1+k_2+k_3=1, \\ k_4+k_5+k_6=1, \\ k_7+k_8+k_9=1. \end{aligned}\right\}. \tag{3}$$

König [37] used the other two conditions to fix the third primary at an imaginary color of dominant wavelength near to that usually corresponding to unitary blue, that is, a stimulus which is perceived under ordinary observing conditions as a blue which is neither reddish nor greenish. In this way König derived the "fundamental sensation" curves incorporated by Ladd-Franklin [41] into her theory of color vision. Following further studies of dichromatic vision, however, König gave up the attempt to make any of the primaries correspond to a unitary hue [38]. In this similar reduction of present-day data on the vision of dichromats, it has likewise seemed advisable to pay no attention to the color perception ordinarily corresponding to the primaries adopted, but rather to strive for the simplest possible adequate representation of the data. Thus, it is possible to satisfy eq 2 and 3 in such a way as to yield wavelength functions for the primaries, each consisting of a curve possessing the single-peak shape of the luminosity function. To avoid functions for W_d and W_p having two maxima, it is sufficient simply to require

$$\left.\begin{aligned} k_3=-0.22\ k_1 \\ k_6=-0.22\ k_4 \end{aligned}\right\} \tag{4}$$

These requirements prevent W_d and W_p from being large near 440 $m\mu$ by utilizing only enough of the Z function to cancel approximately the secondary maximum of the X function in that region.

III. CHROMATICITY CONFUSIONS OF RED-GREEN-BLIND OBSERVERS

As first pointed out by Maxwell, the chromaticity confusions of either type of dichromat may be represented on the chromaticity diagram, or Maxwell triangle, for normal trichromatic vision by a family of straight lines passing through a single point, (x_p, y_p) for the protanope, (x_d, y_d) for the deuteranope. The first determination of these points was that by König and Dieterici [37] based upon two protanopes and two deuteranopes. From these points were derived the "fundamental-sensation" curves (Grund-Empfindungs-Curven) R', G', and B'; and from the approximate relation [30] between these curves and those of the present standard coordinate system for colorimetry, an estimate of the coordinates of the points may be made. From the previously evaluated transformation equations [30, eq 7b] from standard color specifications (X, Y, Z) to (R', G', B') may be found the reverse transformations [30, eq 2]:

$$\left.\begin{aligned} X&=0.244R'-0.058G'+0.014B' \\ Y&=0.056R'+0.150G'-0.005B' \\ Z&=0.000R'+0.000G'+0.200B' \end{aligned}\right\} \qquad (5)$$

By setting $G'=B'=0$ in eq 5, we find $X=0.244R'$, $Y=0.056R'$, $Z=0$, whence:

$$x_p=0.244R'/(0.244R'+0.056R')=0.81$$
$$y_p=0.056R'/(0.244R'+0.056R')=0.19$$

Similarly, by setting $R'=B'=0$, we find $x_d=-0.63$, $y_d=1.63$.

Of course, no very great dependence can be placed on the results of this pioneer work. The connection with the present standard coordinate system is uncertain not only because it is based upon but two partially dark-adapted normal observers (König and Dieterici, who incidentally differed importantly from each other) but also because the basic stimulus of the system ("sunlight reaching the earth's surface through atmosphere of highest transmission") is essentially undefined. If we assume $x=0.33$ and $y=0.34$ for this basic stimulus [46] the protanopic and deuteranopic "neutral" points in the spectrum are found graphically on the (x, y)-plot of the standard ICI system to be 496 and 511 mμ, respectively. This agrees only approximately with the wavelengths (495 and 504 mμ, respectively) read from the König-Dieterici triangle [37, fig. 7] and indicates that the possibilities for considerable error have been realized.

In 1935, however, Pitt [52] published data giving the average chromaticity confusions of eight deuteranopes and seven protanopes in terms of the WDW coordinate system proposed by Wright [59] for visual research because it takes account in a simple way of variations in ocular pigmentation (macula lutea, crystalline lens, humours). From the primaries of this system (spectrum lights at 460, 530, and 650 mμ, respectively) and from the fact that ICI standard illuminant B [23, 27] has in this system for the standard observer the chromaticity coordinates $r=0.249$, $g=0.399$, we may, for the ICI standard

observer, derive equations to connect these chromaticity coordinates (r, g) with those (x, y) of the ICI standard coordinate system:

$$\left.\begin{aligned} x&=\frac{0.874r-0.023g+0.144}{0.402r-0.222g+1.000}\\ y&=\frac{0.354r+0.597g+0.030}{0.402r-0.222g+1.000}\end{aligned}\right\} \quad (6)$$

By means of these equations the chromaticity-confusion lines, shown on Pitt's figures 15 and 16, have been transferred to the ICI system and are shown as dotted lines in figures 1 (a) and 1 (b). It will be noted that the protanope chromaticity confusion lines plotted in figures 1 (a) all run very closely through a single point ($x_p=0.747$, $y_p=0.253$) in conformity to the principle enunciated by Maxwell from the Young theory. The deuteranope chromaticity-confusion lines (figure 1(b)) are not so perfectly copunctal as this, but most of them come fairly close to the point $x_d=1.08$, $y_d=-0.08$.

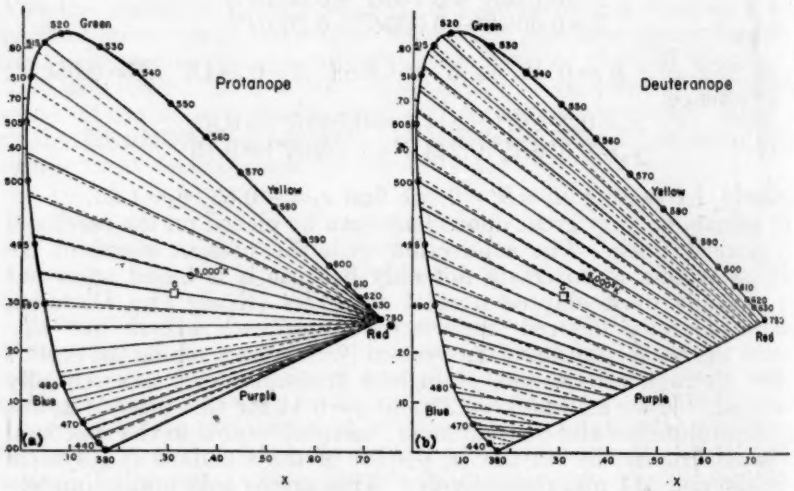

FIGURE 1.—*Chromaticity confusions of the protanope and deuteranope (after Pitt).*

Note how closely the chromaticity-confusion lines (dotted) intersect at a single point for each of the two recognized types of red-green blindness. The solid lines included for comparison are copunctal (protanope at $x=0.747$, $y=0.253$; deuteranope at $x=1.000$, $y=0.000$).

In 1936, Hecht and Shlaer [15] published complete data for two dichromats, one protanope and one deuteranope. These data include luminosity functions, wavelength discrimination, and color-mixture data. The color-mixture data take the form of the energy ratio of two spectral primaries (458.7 and 570.0 mμ) required to produce a chromaticity match for each part of the spectrum. This energy ratio can be accurately defined by the dichromatic observer for the middle portion of the spectrum, but near both 460 and 570 mμ a given energy ratio is found to apply to a considerable spectral range, which

continues to widen as the spectral extremes are approached. Table 1 gives average values of these energy ratios found from the Hecht-Shlaer data taking due account of the rapid decline in the ability of these observers to discriminate wavelength change near 460 and 570mμ. These data may be made independent of the degree of ocular-media pigmentation by transforming them to the red and blue primaries of the *WDW* [59] system. In this system spectral primaries (460 and 650mμ) are used, but, instead of energy units, arbitrary units such as to make the amounts of the primaries equal for 494 mμ are adopted. By the usual methods [26], equations of transformation have been found connecting trichromatic coefficients (r, b) in the *WDW* system to the energy ratios, f_d and f_p, for the protanope *HJ* and the deuteranope *AWG*:

$$\left.\begin{aligned} r&=(0.492-0.003f_p)/(0.492+0.997f_p)\\ b&=f_p/(0.492+0.997f_p)\end{aligned}\right\} \tag{7a}$$

$$\left.\begin{aligned} r&=(31.85-0.021f_d)/(31.85+0.979f_d)\\ b&=f_d/(31.85+0.979f_d)\end{aligned}\right\}. \tag{7b}$$

TABLE 1.—*Comparison of the Hecht-Shlaer color-mixture data for 1 protanope and 1 deuteranope with Pitt's data for 8 protanopes and seven deuteranopes*

Wavelength	Hecht-Shlaer protanope *HJ*		Pitt average protanope, $b=1-r$	Hecht-Shlaer deuteranope *AWG*		Pitt average deuteranope, $b=1-r$
	f_p	$b=1-r$		f_d	$b=1-r$	
mμ						
450	--------	--------	1.03	--------	--------	1.03
460	150.	1.00	1.00	150.	1.00	1.00
470	6.4	0.93	0.93	28.	0.92	0.93
480	2.1	.81	.80	11.2	.79	.80
490	0.77	.61	.57	5.0	.62	.57
500	.294	.37	.34	1.5	.32	.34
510	.100	.17	.17	0.526	.14	.14
520	.033	.06	.09	.182	.05	.06
530	.0113	.02	.06	.062	.02	.03
540	.0040	.01	.04	.025	.01	.02
550	.0005	.001	.02	.010	.003	.01
560	--------	--------	.01	.0025	.001	.00
570	--------	--------	.00	--------	--------	.00
580	--------	--------	.00	--------	--------	.00
590	--------	--------	.00	--------	--------	.00

Table 1 shows the color-mixture data for the protanope *HJ* and the deuteranope *AWG* transformed by eq 7a and 7b to the red and blue primaries of the *WDW* system, and for comparison it also shows the average values found by Pitt [52] for eight protanopes and seven deuteranopes, respectively. It is seen that the Hecht-Shlaer color-mixture data resemble those of Pitt considerably, and comparison of the discrepancies with the known wavelength discrimination of dichromats [15, 52] and with the individual differences among the dichromats studied by Pitt [52, p. 15] shows that the corroboration is wholly satisfactory. It is to be concluded, therefore, that the Hecht-Shlaer data, when referred to the same degree of ocular pigmenta-

tion as is included in the ICI standard observer, indicate the same values of (x_p, y_p) and (x_d, y_d) as the Pitt data.[2]

From figure 1 it may be seen that a source of color temperature 5,000° K ($x=0.344$, $y=0.351$) would possess for an average protanope the same chromaticity as the spectrum at 496 mμ; and for an average deuteranope, the neutral point would be at 500 mμ. As pointed out by v. Kries [38b], a dichromat having ocular-pigmentation heavier than that of the standard observer would have his neutral point shifted toward the long-wave end of the spectrum; for a lightly pigmented dichromat a displacement toward the short-wave end is expected. Wright [59] found that, among the 35 normal observers studied, variations in pigmentation made the point representing 5,000° K vary from ($x=0.29$, $y=0.27$) for no macular pigmentation to ($x=0.39$, $y=0.43$) for the most heavily pigmented observer studied. Table 2 shows the wavelengths of the neutral points to be expected from protanopes and deuteranopes having these extremes of pigmentation, and it also shows for comparison the average and extreme wavelengths of neutral points found by König [35], Pitt [52], and Hecht and Shlaer [15]. The König wavelengths have been increased by 3 mμ for protanopes and 4 mμ for deuteranopes to take account of the chromaticity difference between the average daylight used by him and color temperature 5,000° K. Pitt used illuminant *B* for comparison in determining neutral points; the corrections for the chromaticity difference between this source and one at 5,000° K are negligible and have not been applied. It will be noted from table 2 that the König and Pitt data not only agree in average values with the neutral points read from figure 1, but also fall generally within the limits corresponding to those expected from the pigmentation range of Wright's 35 normal observers. The single deuteranope studied by König who falls slightly outside the pigmentation limits of Wright's 35 normal observers probably corresponds to nothing more than the error of random sampling.

One of the Hecht-Shlaer protanopes and seven of their deuteranopes, however, have neutral points considerably higher than the maximum values corresponding to the most heavily pigmented of Wright's 35 normal observers. That 7 out of 12 deuteranopes are found to have heavier ocular pigmentation than any of 35 normal observers is too much to explain by the error of random sampling. This fact suggests strongly that the populations from which the observers were drawn are significantly different in ocular pigmentation. By this view we must be prepared to accept rather wide individual

[2] Although the color-mixture data for these two dichromats were not put by Hecht and Shlaer into a form suited to prediction of dichromat color matches between heterogeneous stimuli and spectrum stimuli, such a reduction has been carried out recently by Fry [10]. From this reduction it would be possible to determine independently the chromaticity coordinates (x_p, y_p) and (x_d, y_d) of the primary processes not possessed by the two forms of dichromat, instead of relying for this purpose upon Pitt's transformation from the dichromatic to trichromatic diagram of the *WDW* system by determination of the dichromatic luminosities of the primaries. This reduction indicates, however, that the complete radiator at 5,000° K should have had the chromaticity of the spectrum at 498 mμ for protanope *HJ* and 508.5 mμ for deuteranope *A WG*, but by direct observation these wavelengths were found to be 491.5 and 495 mμ, respectively. These discrepancies amount to 5 or 10 times the just noticeable difference for these observers. Although the major part of the discrepancy for protanope *HJ* can be eliminated by more exact methods of reducing the data and by filling in the wavelength region 380 to 470 mμ from Pitt's data, the Hecht-Shlaer data being uncertain in that region, still it would seem that no great reliance is to be placed upon the predictions of dichromat color matches from these data. These discrepancies suggest that the experimental conditions under which the luminosity functions of these observers were obtained may have brought into play a smaller retinal region than that for the color-mixture data, although ostensibly the conditions were identical. Perhaps the mere fact that the luminosity and color-mixture determinations were made separately is a sufficient explanation of the discrepancy. It is doubtful therefore whether separate determination of the copunctal points (x_p, y_p) and (x_d, y_d) from these data would add appreciably to the information obtained by way of the *WDW* coordinate system.

variations in pigmentation. For example, the deuteranope, verified by Hecht and Shlaer as having a neutral point at 525 mμ must have an ocular pigmentation eight or nine times as heavy as the average found by Ludvigh and McCarthy [42] for ocular pigmentation of 62-year-old eyes, excluding the macular pigment. Table 2 also suggests the possibility that deuteranopes tend to have heavier pigmentation than protanopes or normals. It is concluded that individual variations in neutral point are ascribable to variations in ocular pigmentation (macula, lens, humours).

TABLE 2.—*Individual variation in wavelength of neutral point compared to the expected influence of ocular pigmentation based upon 35 normal observers studied by Wright* [59]

Source of data	Number and type of observers	Wavelength in mμ of the spectral region having the dichromatic chromaticity of a source of color temperature 5,000° K					
		Protanope			Deuteranope		
		Minimum	Maximum	Average	Minimum	Maximum	Average
Figure 1	35 normals	489	504	496	494	508	500
König (1884)	7 protanopes, 7 deuteranopes	495	499	497	500	509	503
Pitt (1935)	5 protanopes, 6 deuteranopes	494	497	496	495	507	500
Hecht-Shlaer (1936)	10 protanopes, 12 deuteranopes	492	508	498	491	525	510

IV. DERIVATION OF RESPONSE FUNCTIONS

It is worth noticing that the point (x_p=0.747, y_p=0.253) found from Pitt's data as the common crossing point of the protanopic chromaticity-confusion lines is very close to the long-wave extreme of the spectrum (x=0.735, y=0.265) used as a primary in the OSA coordinate system [57]. Reference to figure 1(a) shows immediately that in spite of this close approach, the long-wave extreme of the spectrum is not eligible to represent (x_p, y_p). For example, the line connecting the extremes of the spectrum cuts all of the protanopic chromaticity-confusion lines (dotted); that is, the protanopic chromaticity of the long-wave extreme differs maximally from that of the short-wave extreme. But if the long-wave extreme of the spectrum locus were itself taken as the point (x_p, y_p), one interpretation would be that the two extremes of the spectrum have the same protanopic chromaticity. On this account the solid lines of figure 1(a) drawn in for comparison have been made copunctal at (x_p=0.747, y_p=0.253). Although the choice of the long-wave extreme of the spectrum to represent (x_p, y_p) flatly contradicts the facts, it is of interest to inquire what response functions are generated by this choice, because it bears on a question raised in 1798 by Dalton [3] and argued many times since, namely: Are protanopes red-blind?

Similarly, it is worth noting that the point (x_d=1.08, y_d=−0.08) estimated from Pitt's data as the most probable common crossing point of the deuteranopic chromaticity-confusion lines is fairly close to the X primary (x=1.00, y=0.00) of the standard ICI coordinate system. The solid lines of figure 1 (b) have been drawn through this

point, and it is seen that with one exception the solid lines are either closely parallel to the nearest dotted line or cross a single dotted line. Since the separation of the dotted lines indicates the smallest chromaticity difference perceptible to Pitt's observers, it may be concluded that to set $x_d=1$ and $y_d=0$ is not inconsistent with these data; and, indeed, from a set of lines drawn through the point ($x_d=1.08$, $y_d=-0.08$) it may be concluded that the former choice is scarcely less apt than the latter, which was chosen as the best estimate possible. It will be of interest, therefore, to study both choices.

It is convenient to start this study by investigating the implications of setting $x_p+y_p=x_d+y_d=1$, or, stated another way, since $z=1-x-y$, the implications of setting $z_p=z_d=0$. All four points under consideration meet this requirement.

If $z_p=z_d=0$, from eq 2a and 2b, we find $k_7=k_8=0$, provided $x_p/y_p\neq x_d/y_d$, that is, provided (x_p, y_p) and (x_d, y_d) are different points; and from eq 3, we find that $k_9=1$. From eq 1 we may therefore write $K=Z$. This conclusion is important. It says that since both the protanopic chromaticity-confusion lines and the deuteranopic-confusion lines are copunctal at points lying on the tangent to the spectrum locus at the long-wave extreme, the Z function of the standard observer is adequate to represent the K function used in describing the chromaticity confusions of both deuteranope and protanope. König [37], from somewhat incomplete data [6], drew this conclusion, and v. Kries [39, p. 164] deduced it from the identity of the K function of protanope and deuteranope on the assumption that both are reduction forms of normal vision.

A further conclusion is possible from setting $z_p=z_d=0$. From eq 2b, 3, and 4, we may write three simultaneous equations with only three unknowns, thus

$$\begin{aligned} k_1x_d+k_2y_d&=0\\ k_1+k_2+k_3&=1\\ k_3&=-0.22k_1, \end{aligned}$$

from which the coefficients, k_1 to k_3, defining the W_d function by eq 1, are found to be

$$k_1=-y_d/(x_d-0.78y_d),\ k_2=x_d/(x_d-0.78y_d),\ k_3=0.22y_d/(x_d-0.78). \quad (8a)$$

Thus it is seen that the W_d function (warm curve of deuteranopes) is determined wholly by the coordinates of the point (x_d,y_d) provided $z_d=z_p=0$, as they do for the four choices of interest.

Similarly, from eq 2a, 3, and 4, we find that

$$k_4=-y_p/(x_p-0.78y_p),k_5=x_p/(x_p-0.78y_p),k_6=0.22y_p/(x_p-0.78y_p). \quad (8b)$$

Thus it is seen that the W_p function (warm curve of protanopes) is determined wholly by the coordinates of the point (x_p, y_p), again provided $z_d=z_p=0$.

The next step is to find the response functions resulting from setting $x_d=1$, $y_d=z_d=0$, as is justified from available data on chromaticity confusions of deuteranopes. From eq 8a, we find immediately that $k_1=k_3=0$, and $k_2=1$. Hence from eq 1, $W_d=Y$. This conclusion is important. It says that since the deuteranopic chromaticity-confusion lines may be taken as copunctal at $x_d=1$, $y_d=z_d=0$, then the Y function of the standard observer is adequate to represent

the W_d function (warm curve of the deuteranope) for describing the chromaticity confusions of the deuteranope. The great convenience of being able to use two (Z and Y) of the three functions representing the standard observer directly in deuteranopic chromaticity specifications should be emphasized. It means that the chromaticity of any color stimulus already specified in terms of the standard observer may be specified for an average deuteranope merely by leaving the X-specification out of account. That is, any two stimuli for which the Y-specification and the Z-specification bear the same ratio will be chromaticity matches for an average deuteranope.

The W_p function is found from the values of $x_p=0.747$, $y_p=0.253$, through eq 8b and 1, to be

$$W_p=-0.460X+1.359Y+0.101Z. \tag{9}$$

The W_p function generated from the theoretically interesting but factually inadmissible values of $x_p=0.735$, $y_p=0.265$ is found in a similar way to be

$$W'_p=-0.503X+1.392Y+0.111Z. \tag{9a}$$

The W_d function agreeing as closely to the Pitt average data as is possible ($x_d=1.08$, $y_d=-0.08$, $z_d=0.00$) is found from eq 8a and 1 to be

$$W'_d=0.079X+1.061Y-0.017Z. \tag{10}$$

V. LUMINOSITY FUNCTIONS OF RED-GREEN-BLIND OBSERVERS COMPARED TO THOSE OF NORMAL AND ANOMALOUS TRICHROMATS

We may now inquire into the relationship between the functions, W_d, W_p, W'_d, and W'_p, and the luminosity functions of dichromatic and trichromatic observers. Figure 2 shows, by dotted lines, the luminosity functions of eleven protanomalous observers studied by McKeon and Wright [45] and one studied by Nelson [49]. It also shows by solid lines the luminosity functions of six deuteranomalous observers studied by Nelson [49]. Although at the short-wave end of the spectrum these groups of functions overlap and are not significantly different, the two groups divide quite sharply at the long-wave end. In this respect they are like the groups of functions representing the two corresponding types of dichromatic observer, the deuteranope and the protanope. The circles represent the average of six protanopic luminosity functions evaluated by Pitt [52], and the crosses represent his average of six deuteranopic luminosity functions. The arrows indicate the maximum and minimum values of relative luminosity found by Gibson and Tyndall [11] among their 37 completely studied normal observers. Although because of differences in experimental conditions no highly precise intercomparison is possible between the data shown for anomalous and dichromatic observers and these normal limits, nevertheless figure 2 indicates that the deuteranopic and deuteranomalous observers alike possess luminosity functions generally well within normal limits; but both protanomalous observers and protanopic observers possess luminosity functions that are anbormally low at the long-wave end.

Figure 2 tends to indicate also that protanomalous observers possess abnormally narrow luminosity functions even compared to protanopes, and that deuteranopes possess luminosity functions abnormally high between 570 and 610 mμ with deuteranomalous observers intermediate in this respect; but because of the small number of abnormal observers tested, these indications may fail to be significant. The experimental conditions (field size, field luminance, surrounding-field luminance) and technics (adaptation, control of fixation, length of observing time) govern the participation of the rod mechanism in determining these functions. In any one study the luminosity curves may be thrown more or less to the short-wave side because of partial participation of the rods, either intended or inadvertent. The intertwining

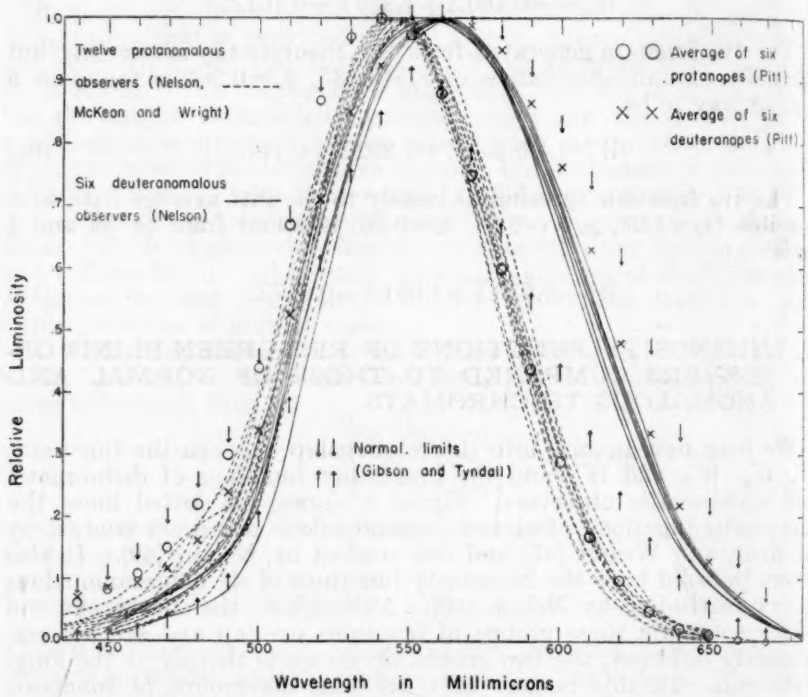

FIGURE 2.—*Relative luminosity functions of anomalous trichromats (6 deuteranomalous, 12 protanomalous) compared to averages for dichromats and to limits for normal trichromats.*

Deuteranopic and deuteranomalous luminosity functions fall generally within normal limits, but protanopic and protanomalous luminosity functions fall outside of normal limits.

of the curves at the short-wave end is probably to be ascribed chiefly to individual variation in the amount of yellow or brown pigmentation of the eye media, such as degree of macular pigmentation.

Since from figure 2 both deuteranopic and deuteranomalous luminosity functions fall generally within the limits of 37 normal observers, it is just as valid to predict the brightness judgments of these abnormal observers from the standard luminosity function as it is those of an observer chosen at random from the large population group to be classed as of normal color vision. Figure 3 compares the standard

luminosity function, $Y=W_d$, (dotted line) with the upper and lower limits (arrows) for the deuteranopic and deuteranomalous luminosity functions referred to in figure 2. The standard luminosity function is seen to fall satisfactorily within these limits except for the wavelength region between 570 and 610mμ. Studies by Sloan [56], corroborated by the recent work of Walters and Wright [58], show that the shape of the luminosity function within this wavelength region is particularly subject to variation with experimental conditions. It is therefore perhaps reasonable to ascribe the whole of this small discrepancy to variation in experimental conditions.

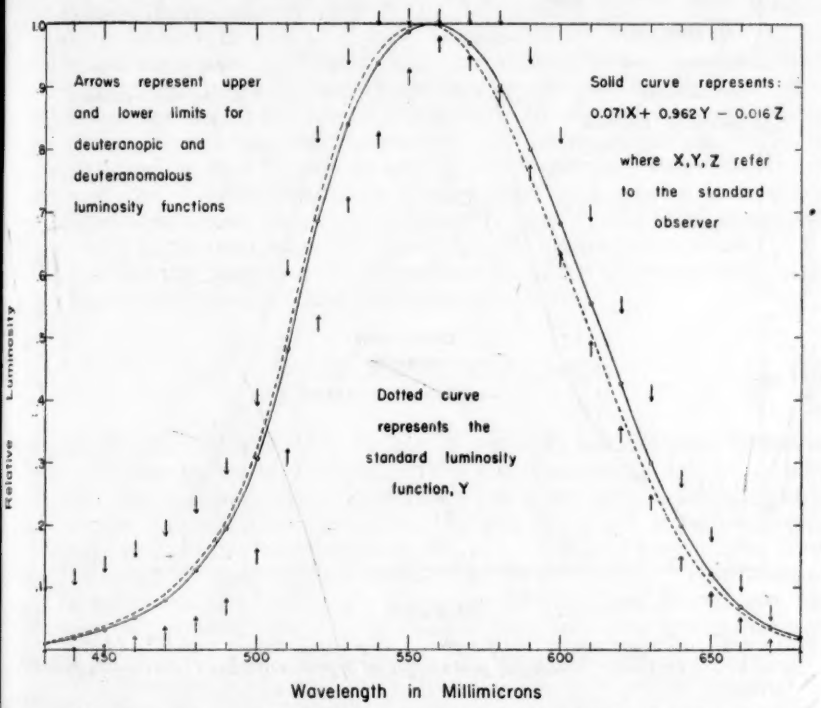

FIGURE. 3.—*Comparison of the functions W'_d (standard luminosity function, Y) and W'_d (solid curve) with upper and lower limits for deuteranopic and deuteranomalous luminosity functions (arrows).*

The standard luminosity function is seen to fall satisfactorily within these limits except for the wavelength region between 570 mμ and 610 mμ. The function W'_d yields slightly better agreement.

Figure 3 also shows the function W'_d (eq 10) adjusted to unit maximum as a solid line. This function represents available data on deuteranopic luminosity slightly better than the standard luminosity function $Y=W_d$, just as, combined with the K function, it represents deuteranopic chromaticity data slightly better. There is therefore some basis for arguing, as in the most common form of Young-Helmholtz theory, that the normal luminosity function should be thought of as consisting of three components, a red, a green, and a violet.[3] Whether this possible justification of the usual Young-

[3] An account of dichromatic vision following this view has recently been worked out by Pitt [53].

Helmholtz view would be borne out by a study of an adequate sample of normal and deuteranopic observers remains to be decided by further extensive experiment. The two functions, W_d and W'_d, differ so little, however, that it would rarely be of practical importance to use one rather than the other. Because of its greater simplicity it seems better to take $W_d = Y$ as the function representing deuteranopic and deuteranomalous luminosity.

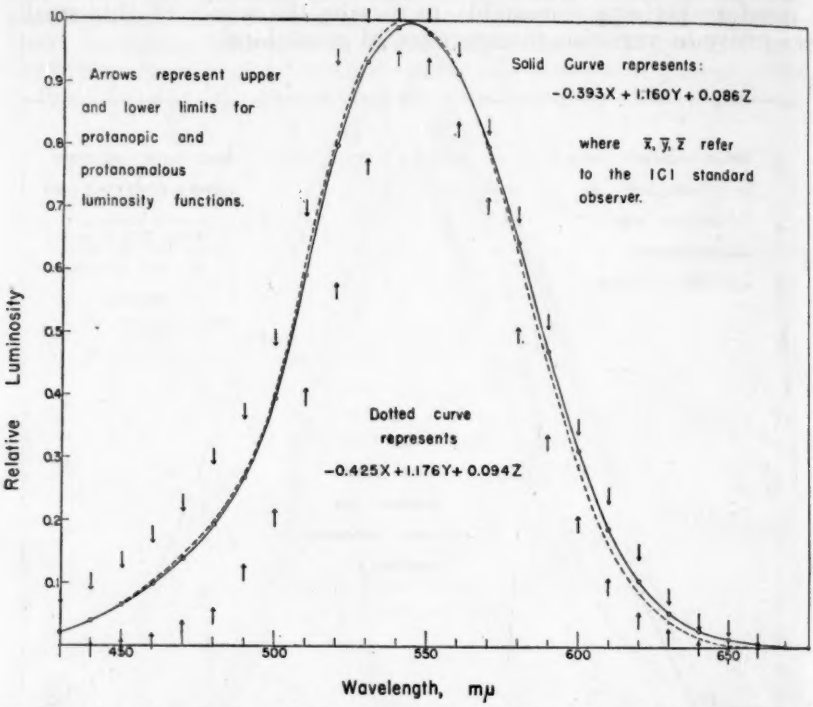

FIGURE 4.—*Comparison of the functions W_p (solid curve) and W'_p (dotted curve) with upper and lower limits for protanopic and protanomalous luminosity functions (arrows).*

Both functions are seen to fall satisfactorily within these limits, except that W'_p is perhaps too low for wavelengths greater than 650 mμ.

Figure 4 compares the functions 0.854 W_p and 0.845 W'_p with the upper and lower limits (arrows) for the protanopic and protanomalous luminosity functions referred to in Figure 2. The constants 0.854 and 0.845 serve to adjust the functions approximately to unit maximum, and from eq 9 and 9a, respectively yield

$$0.854\ W_p = -0.393X + 1.160Y + 0.086Z \text{ (solid curve)},$$
$$0.845\ W'_p = -0.425X + 1.176Y + 0.094Z \text{ (dotted curve)}.$$

It is seen that both functions fall satisfactorily between the limits at least for wavelengths shorter than 650 mμ. The function W_p, therefore, not only represents adequately, when combined with the K function, the chromaticity confusions of the average protanope, but also, taken by itself, his brightness judgments. The function W'_p,

although it grossly fails, when combined with the K function, to represent the chromaticity confusions of the protanope, nevertheless succeeds in representing adequately his brightness judgments except for wavelengths greater than 650 mμ. This rather minor difference in luminosity function is all that differentiates red-blind vision (luminosity zero for wavelengths greater than 700 mμ) from the experimentally determined facts of protanopia. The old name, red blindness, is therefore nearly but not quite accurate.

By way of contrast it may be pointed out that the corresponding old name, green blindness, for the type of defect known since v. Kries [46] as deuteranopia is almost wholly wrong. Since the standard luminosity function represents the brightness judgments of deuteranopic observers just as closely as those of a considerable fraction of normal observers, and is far from being zero anywhere within the spectrum region that ordinarily appears green (490 to 550 mμ), deuteranopes are far from being insensitive to the green part of the spectrum. It is true that protanopia and deuteranopia can logically be described as red blindness and green blindness, respectively, in terms of the Young-Helmholtz theory, but in a purely descriptive nontheoretical sense, no observer has ever been found to be quite red-blind, and none even remotely deserving the name green-blind.

The following functions therefore may be taken to be representative of normal, deuteranopic and protanopic vision:

$$\left.\begin{aligned} K&=Z \\ W_p&=-0.460X+1.359Y+0.101Z \\ W_d&=Y \end{aligned}\right\} \tag{11}$$

K and W_d for deuteranopic vision, K and W_p for protanopic vision, and all three for normal vision. It is also true, although no adjustments other than eq 4 have been made for it nor any detailed quantitative comparisons presented, that W_p and W_d taken together closely represent tritanopic vision [31, 33, 38, 47]. Table 3 gives these three functions for 10-mμ intervals of the visible spectrum. The function W_p is taken as the luminosity function of a typical protanope, the function W_d is taken as the luminosity function of a typical deuteranope as well as the normal observer (and perhaps also that of a typical tritanope [7, 8, 34]), and the function K is unassociated with luminosity.

The representation of normal vision by K, W_d, and W_p is just as adequate as that afforded by the functions Z, Y, and X of the standard ICI coordinate system, and indeed functions closely like these were proposed by the author in 1931 for international adoption through the American representative, Irwin G. Priest, but were rejected because the corresponding chromaticity diagram gave considerably less uniform chromaticity scales than the coordinate system (X, Y, Z) finally adopted. There is therefore nothing to be gained by supplanting the present X-function by W_p to represent normal vision, and this substitution is not recommended.

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TABLE 3.—*Response functions for protanopic (W_p, K) and deuteranopic (W_d, K) vision*

Wavelength	W_d	W_p	K	Wavelength	W_d	W_p	K
mμ				mμ			
380	0.00004	0.00006	0.0065	600	0.6310	0.3690	0.0008
390	.00012	.00024	.0201	610	.5030	.2224	.0003
				620	.3810	.1248	.0002
400	.0004	.00082	.0679	630	.2650	.0646	.0000
410	.0012	.00257	.2074	640	.1750	.0318	.0000
420	.0040	.00883	.6456				
430	.0116	.0251	1.3856	650	.1070	.0150	.0000
440	.0230	.0476	1.7471	660	.0610	.0070	.0000
				670	.0320	.0033	.0000
450	.0380	.0759	1.7721	680	.0170	.00157	.0000
460	.0600	.1163	1.6692	690	.0082	.00070	.0000
470	.0910	.1638	1.2876				
480	.1390	.2270	0.8130	700	.0041	.00035	.0000
490	.2080	.3150	.4652	710	.0021	.00018	.0000
				720	.00105	.000089	.0000
500	.3230	.4642	.2720	730	.00052	.000044	.0000
510	.5030	.6953	.1582	740	.00025	.000021	.0000
520	.7100	.9437	.0782				
530	.8820	1.0997	.0422	750	.00012	.000010	.0000
540	.9540	1.1650	.0203	760	.00006	.000005	.0000
				770	.00003	.000003	.0000
550	.9950	1.1537	.0087				
560	.9950	1.0791	.0039				
570	.9520	0.9434	.0021				
580	.8700	.7610	.0017				
590	.7570	.5568	.0011				

The representation of deuteranopic vision by K and W_d, and protanopic vision by K and W_p, is valid in the same way as representation of normal vision by X, Y, and Z. No single normal observer, or protanope, or deuteranope, can be found, except by accident, who conforms to the standard representation of the respective group, but the departures of each single individual from the standard may be expected to be smaller than some of the individual differences within the group.

VI. USE OF THE RESPONSE FUNCTIONS

The response functions K, W_p, and W_d have been used by the ISCC Committee on Colorblindness [4] to find whether or not two colors will be confused by an average protanope or an average deuteranope. Such use will be illustrated by solution of three problems: First, what is the influence of the choice of standard neutral source on the dichromatic neutral points in the spectrum; second, how much darker to an average protanope are normally reddish colors; and third, what arrangements of the colors of the Farnsworth dichotomous test B–20 [9] are characteristic of average deuteranopic and protanopic vision.

1. WAVELENGTH OF NEUTRAL POINT

The determination of the neutral point in the spectrum of a dichromatic observer involves setting up a chromaticity match between some standard neutral source (ICI illuminant A, ICI illuminant C, black-body at 5,000 ° K, and so forth) and some part of the spectrum (see table 2). Deuteranopic and protanopic chromaticity is conveniently specified by chromaticity coordinates w_d, k_d and w_p, k_p, the

[4] Committee on Colorblindness Tests, Inter-Society Color Council, Co-Chairmen LeGrand H. Hardy and the author.

first pair for deuteranopic vision, the second for protanopic. The definitions of these coordinates and their equivalents in terms of X, Y, Z, from eq 11 are as follows:

$$\left.\begin{aligned} w_d &\equiv W_d/(W_d+K)=Y/(Y+Z) \\ k_d &\equiv K/(W_d+K)=Z/(Y+Z) \end{aligned}\right\} \tag{12a}$$

$$\left.\begin{aligned} w_p &\equiv W_p/(W_p+K)= \frac{-0.460X+1.359Y+0.101Z}{-0.460X+1.359Y+1.101Z} \\ k_p &\equiv K/(W_p+K)=Z/(-0.460X+1.359Y+1.101Z) \end{aligned}\right\} \tag{12b}$$

Table 4 shows these coordinates for the various parts of the spectrum, particularly the portions near 495 mμ where chromaticity for these types of dichromatic vision varies most rapidly with wavelength. Since from their definitions the two coordinates sum to unity, only one of them is required to specify the dichromatic chromaticity of a stimulus.

TABLE 4.—*Chromaticity coordinates for deuteranopic and protanopic vision*

Wavelength	Chromaticity coordinates			
	Protanopia		Deuteranopia	
	w_p	k_p	w_d	k_d
mμ				
380	0.012	0.988	0.006	0.994
430	.018	.982	.008	.992
450	.041	.959	.021	.979
460	.065	.935	.035	.965
470	.113	.887	.066	.934
475	.156	.844	.098	.902
480	.218	.782	.146	.854
485	.301	.699	.216	.784
490	.404	.596	.309	.691
495	.518	.482	.423	.577
500	.631	.369	.543	.457
505	.730	.270	.657	.343
510	.815	.185	.761	.239
515	.881	.119	.845	.155
520	.923	.077	.901	.099
530	.963	.037	.953	.047
540	.982	.018	.979	.021
550	.992	.007	.991	.009
600	.998	.002	.999	.001
650	1.000	.000	1.000	.000
750	1.000	.000	1.000	.000

In order to find the neutral point in the spectrum of, say, an average protanope for a standard neutral source specified in the standard ICI system by X_o, Y_o, Z_o, it is necessary only to compute w_p from eq 12b and find by interpolation among the values of w_p for the spectrum given in table 4, the wavelength for the corresponding value. This wavelength corresponds to the same chromaticity as the standard neutral source and is therefore the desired neutral point. This method is the analytic equivalent of a graphical method using the chromaticity diagram of the standard system (see fig. 1). The graphical method is to draw a straight line from the copunctal point through the point

representing the chromaticity of the standard neutral source and extend it until it cuts the spectrum locus. The wavelength corresponding to this intersection is the desired neutral point in the dichromatic spectrum.

Table 5 gives the standard chromaticity specifications, x and y, for several sources that might be taken as standard neutrals, the values of w_p and w_d for these sources, and the corresponding neutral points found by the analytical method from table 4. It will be noted that the change in neutral point depending upon choice of standard neutral source is considerably greater than the difference between the neutral points of the typical protanope and typical deuteranope for any one source.

TABLE 5.—*Protanopic and deuteranopic neutral points in the spectrum derived from the dichromatic chromaticity coordinates, w_p and w_d*

Standard source	ICI chromaticity coordinates		Dichromatic chromaticity coordinates		Wavelength of the neutral point	
	x	y	w_p	w_d	λ_p	λ_d
					mμ	mμ
ICI illuminant *A*	0.4476	0.4075	0.7144	0.7377	504.0	508.9
ICI illuminant *B*	.3484	.3516	.5369	.5396	495.8	499.8
Complete radiator at 5,000° K	.3445	.3512	.5346	.5358	495.7	499.7
ICI illuminant *C*	.3101	.3163	.4652	.4585	492.7	496.6
Illuminant *D* [1]	.2999	.3120	.4559	.4457	492.3	495.8
Illuminant *S* [2]	.2319	.2318	.3286	.3018	486.4	489.6

[1] Illuminant *D* is produced by an incandescent lamp and Corning Daylite glass filter [32, p. 60] and has a nearest color temperature [28] of about 7,500° K.

[2] Illuminant *S* was found [32, p. 58] by weighting Abbot's "sun-outside-atmosphere" energy data by the inverse λ^4 scattering relation, and has been designated as "limit blue sky."

2. PROTANOPIC LUMINOUS REFLECTANCE

The second problem is to find how much darker to an average protanope are normally reddish colors. For spectrum colors the solution is given simply by comparing W_p with $Y=W_d$ in table 3. It is seen, for example, that relative to an equal-energy source, an average protanope finds the spectrum from 700 to 770 mμ to have less than 10 percent of the normal luminosity. It could be said therefore in a sense that he is more than 90-percent blind to the long-wave end of the spectrum; but we would also have to say in the same sense that he is supersensitive by a factor of 2 for the spectral region near 450 mμ. It is more convenient to say that the luminosity function of the average protanope is shifted about 10 mμ toward the short-wave end of the spectrum relative to normal.

If the color is that of a surface, it is customary to estimate its lightness or darkness from the luminous reflectance of the surface for ICI illuminant *C* relative to magnesium oxide. For magnesium oxide, $X=0.9804$, $Y=1.0000$, and $Z=1.1812$, and from eq 9, $W_p=1.0274$. Protanopic luminous reflectance relative to magnesium oxide is therefore equal to $W_p/1.0274$ or $0.9733\ W_p$. It is convenient to represent on the (x, y) chromaticity diagram the dependence of protanopic luminous reflectance of a surface on the normal chromaticity of its color.

If Q be the ratio of the protanopic luminous reflectance of a surface to its normal luminous reflectance, Y, we may write

$$Q=0.9733\ W_p/Y=0.9733\ (-0.460X+1.359\ Y+0.101\ Z)/Y$$
$$=0.9733\ (-0.460\ x+1.359\ y+0.101\ z)/\ y$$

whence it is found

$$x=y(Q-1.224)/(-0.546)+0.180. \qquad (13)$$

Examination of eq 13 shows that it represents a family of straight lines on the (x, y) chromaticity diagram passing through the point (x=0.180, y=0.000). For Q=1, the line passes through the point representing illuminant C (x=0.3101, y=0.3163). All surfaces

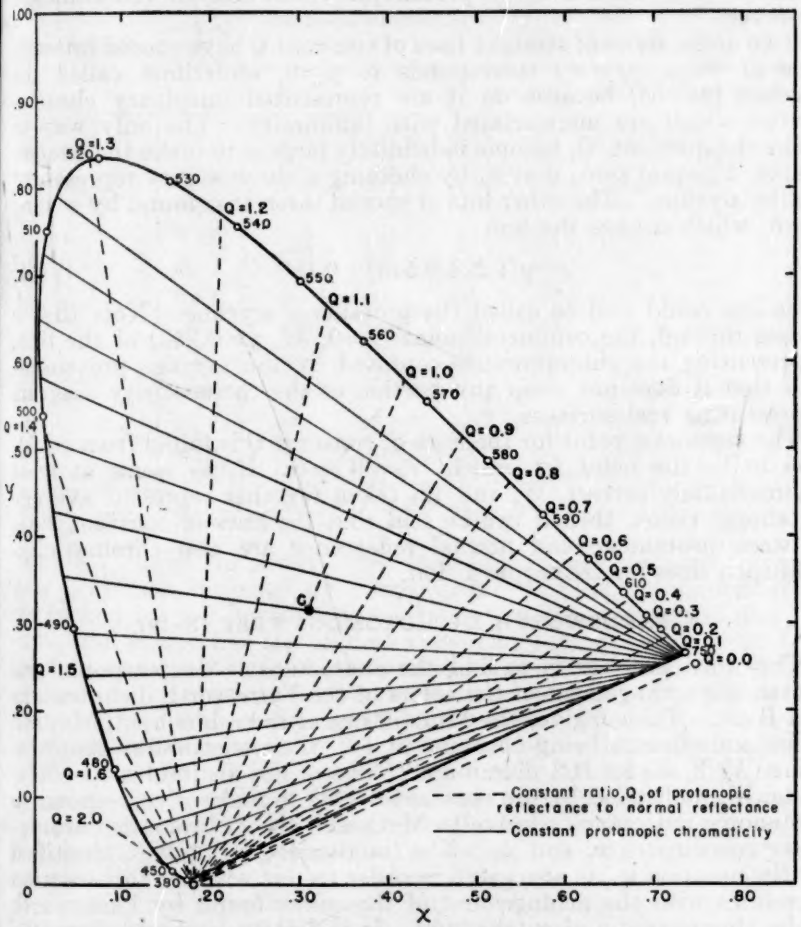


FIGURE 5.—*Relation of protanopic to normal vision.*

The solid lines (as in fig. 1) represent constant protanopic chromaticity; the dotted lines represent constant values of the ratio, Q, of protanopic luminous reflectance to normal luminous reflectance. Both reflectances are taken relative to that of magnesium oxide and refer to ICI standard illuminant C. Note that the line (dotted) for Q=1 passes through the point x=0.310, y=0.316, representing illuminant C. Note also that the line for Q=0 passes through the copunctal point x=0.747, y=0.253; this line could be called the protanopic alychne (lightless line), just as the line for $Q=\infty$ (y=0, see eq 13) has sometimes been called the normal alychne.

whose chromaticities under illuminant C are represented on this line have identical protanopic and normal luminous reflectances. For $Q=2.0$, the line passes close to 450 mμ; all surfaces represented on this line have protanopic luminous reflectance twice the normal luminous reflectance. For $Q=0.10$, the line passes close to 650 mμ; all surfaces represented on this line have protanopic luminous reflectance equal to 10 percent of the normal luminous reflectance. Figure 5 shows a number of these lines of constant Q (dotted) on the (x, y) chromaticity diagram; it indicates completely and quantitatively how much darker to an average protanope are normally reddish colors. It also shows the lines of protanopic chromaticity confusion; it therefore gives a convenient, concise and quantitative summary of the connection between average protanopic vision and the ICI standard observer.

Two of the series of straight lines of constant Q have special interest. One of them ($Q=\infty$) corresponds to $y=0$, sometimes called the alychne [25, 55] because on it are represented imaginary chromaticities which are unassociated with luminosity. The only way to make the quotient, Q, become indefinitely large is to make the denominator, Y, equal zero; that is, by choosing a chromaticity represented on the alychne. The other line of special interest is found by setting $Q=0$, which defines the line

$$x=y(1.224/0.546)+0.180. \tag{14}$$

This line could well be called the protanopic alychne. Note that it passes through the copunctal point ($x=0.747$, $y=0.253$) of the lines representing the chromaticities confused by the average protanope, and that it does not cross any portion of the chromaticity diagram representing real surfaces.

The copunctal point for the lines of constant Q is found from eq 11, also to be the point for which $W_d=W_b=0$. If, as seems at least approximately correct, W_d and W_b taken together represent average tritanopic vision, then it can be said that the lines of constant ratio between protanopic and normal reflectance are also chromaticity-confusion lines for tritanopic vision.

3. FARNSWORTH DICHOTOMOUS TEST (B–20)

The third problem is to find the characteristic deuteranopic and protanopic arrangement of the colors of the Farnsworth dichotomous test B–20. Table 6 gives the Munsell hue of the colors used, Munsell value and chroma being constant at 5/2, their tristimulus specifications (X, Y, Z) for ICI illuminant C, one of the distimulus specifications, W_p multiplied by the constant 0.9733 to make it correspond to protanopic reflectance relative to MgO, and the dichromatic chromaticity coordinates w_p and w_d. The fraction $W_d/(W_p+W_d)$, identified by the notation w_t, is also given in order to test whether this fraction correlates with the arrangement of the colors found by Farnsworth to be characteristic of a tritanope. It is first to be noted from the relative constancy of the daylight reflectance, $w_d=Y$, and the protanopic reflectance, $0.9733W_p$, for these colors that the papers used in the Farnsworth dichotomous test have nearly the same reflectances for illuminant C not only for the standard observer and typical deuteranope ($W_d=Y$), but also for the typical protanope ($0.9733W_p$)

the variation being between 0.2321 and 0.1818 which correspond to only 0.55 of a Munsell value step [50]. Since these papers are exhibited with a dark-gray border that interferes with perception of lightness differences more than it does chromaticity differences [29, p. 425] the basis for arranging the colors in order must be chiefly according to chromaticity. The characteristic protanopic arrangement is therefore to be found in accord with w_p, and the characteristic deuteranopic arrangement according to w_d.

TABLE 6.—*Tristimulus and distimulus specifications of the colors of the Farnsworth dichotomous test for color vision*

Serial number	Munsell hue (at 5/2)	Tristimulus specifications			Protanopic reflectance	Distimulus chromaticity coordinates		
		X	Y	Z	$0.9733\,W_p$	w_p	w_d	w_t
1	10B	0.2121	0.2229	0.3292	0.2321	0.4201	0.4037	0.4831
2	5B	.1749	.1917	.2831	.2030	.4242	.4037	.4789
3	10BG	.1820	.2043	.2790	.2162	.4432	.4227	.4791
4	5BG	.1782	.2077	.2538	.2199	.4709	.4501	.4790
5	5G	.1618	.1888	.2017	.1972	.5011	.4835	.4824
6	10GY	.1766	.2017	.1873	.2061	.5307	.5185	.4878
7	5GY	.1908	.2097	.1804	.2096	.5442	.5376	.4933
8	10Y	.2135	.2292	.1798	.2253	.5628	.5604	.4975
9	5Y	.2057	.2117	1795	.2056	5406	.5412	.5006
10	10YR	.2170	.2143	.1780	.2038	.5405	.5463	.5058
11	5YR	.2029	.1927	.1755	.1813	.5149	.5234	.5084
12	10R	.2364	.2185	.2055	.2034	.5042	.5153	.5111
13	5R	.2158	.1954	.2041	.1818	.4779	.4891	.5113
14	10RP	.2426	.2229	.2453	.2103	.4684	.4761	.5077
15	5RP	.2304	.2138	2559	.2048	.4512	.4552	.5040
16	10P	.2256	.2092	.2751	.2027	.4309	.4320	.5011
17	5P	.2070	.1959	.2818	.1942	.4145	.4101	.4954
18	10PB	.2199	.2118	.3301	.2140	.3998	.3908	.4906
19	7.5PB	.2055	.2035	.3036	.2071	.4121	.4013	.4882
20	5PB	.2052	.2087	.3277	.2164	.4042	.3891	.484

Table 7 shows the serial order according to w_p compared to that for a protanope reported by Farnsworth. That is, color number 8 was picked by the Farnsworth protanope as the warmest of the 20 colors, and it also has the highest value of w_p (0.5628 from table 5); therefore number 8 heads both the second and third column of table 6. A similar comparison is given between the arrangements according to w_d and a deuteranope reported by Farnsworth, and between w_t and the tritanope reported by Farnsworth. It is evident from table 7 that the correlations indicated by these comparisons are high; that is, the results chosen by Farnsworth to be typical of protanopia, deuteranopia, and tritanopia agree well, though not perfectly, with the chromaticity arrangements according to w_p, w_d, and w_t, respectively.

Failure of the agreement to be perfect might be due to failure of the tristimulus specifications reported for certain samples of the Munsell papers to apply exactly to the particular samples used in the Farnsworth test B–20, to careless arrangement of the colors by the dichromatic observer or to arrangement on a basis other than chromaticity, or to significant difference between the visual system of the dichromat and that represented by the pairs of functions, K, W_p,

and W_d taken here to represent the average protanope and deuteranope. By plotting the orders given in table 7 according to w_p, w_d, and w_t on the Farnsworth chart for analysing results on the dichotomous test (see his fig. 15), it is discovered that most of the minor differences are ascribable to a real difference between the typical Farnsworth dichromats and the corresponding hypothetical observers defined by the functions K, W_p, and W_d. The axes of confusion for the hypothetical observers fall, however, within the limits indicated by Farnsworth (see his fig. 15) as embracing the three types of dichromat delineated by the dichotomous test.

TABLE 7.—*Comparison of serial orders of the colors of the Farnsworth dichotomous test according to w_p, w_d, and w_t with the orders reported by Farnsworth for a protanope (red-bluegreen confuser), and deuteranope (green-redpurple confuser), and a tritanope (violet-greenishyellow confuser)*

Normal order (based on hue)	Serial numbers in order from warmest to coldest dichromatic color according to—					
	w_p	Farnsworth protanope	w_d	Farnsworth deuteranope	w_t	Farnsworth tritanope
1	8	8	8	10	13	13
2	7	10	10	9	12	14
3	9	7	9	8	11	15
4	10	6	7	7	14	12
5	6	9	11	11	10	11
6	11	11	6	12	15	16
7	12	5	12	6	16	10
8	5	12	13	13	9	9
9	13	13	5	14	8	17
10	4	4	14	5	17	18
11	14	3	15	15	7	8
12	15	15	4	16	18	19
13	3	14	16	4	19	7
14	16	2	3	17	6	20
15	2	16	17	3	20	1
16	1	17	2	2	1	6
17	17	1	1	18	5	2
18	19	19	19	20	3	5
19	20	20	18	19	4	4
20	18	18	20	1	2	3

Although this corroboration was expected for protanopic and deuteranopic vision because of the firm basis for choosing the functions K, W_p, and W_d, it is interesting to note that substantially the same agreement is found for tritanopic vision. The discrepancies are of the sort to be ascribed to individual differences. It is evident that the Farnsworth test is well adapted for surveys of the characteristics of dichromats; a statistical treatment of an extended body of data found by this test would serve to determine whether the functions proposed here for dichromatic vision describe, as was intended, visual systems intermediate to actual observers of the corresponding type; also whether the functions W_p and W_d, taken together, describe a type of tritanopic vision intermediate to actual tritanopes.

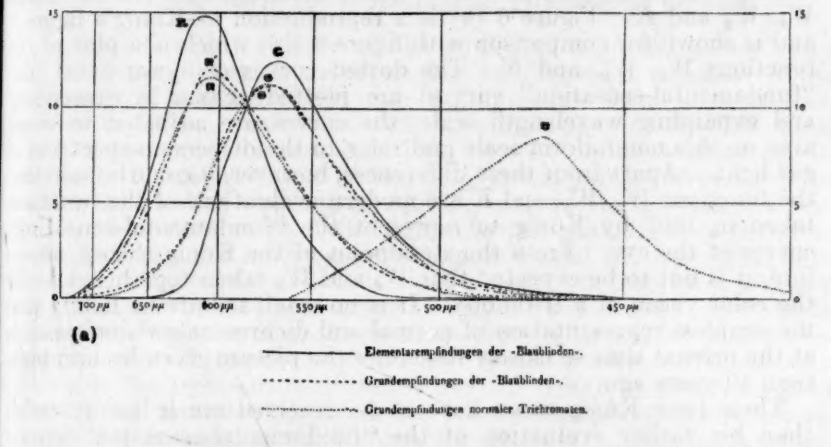
VII. THEORETICAL IMPLICATIONS OF THE RESPONSE FUNCTIONS

The functions W_d, W_p, and K defined in eq 11 have theoretical implications, the validity of which in no way interferes with the practical applications just discussed. It is convenient to bring out

these implications by indicating the relation of these functions to the later theoretical views of Arthur König, to the recent dominator-modulator theory of Granit, and to the zone-theory of G. E. Müller.

1. KÖNIG THEORIES

In 1886 and in 1893 Arthur König published accounts of his monumental work on the color systems of normal and abnormal observers [36, 37]. The coordinate system chosen by him to represent his experimental results satisfies eq 1 and 2 but does not satisfy eq 4, since one of the "fundamental sensations" was taken as unitary blue.



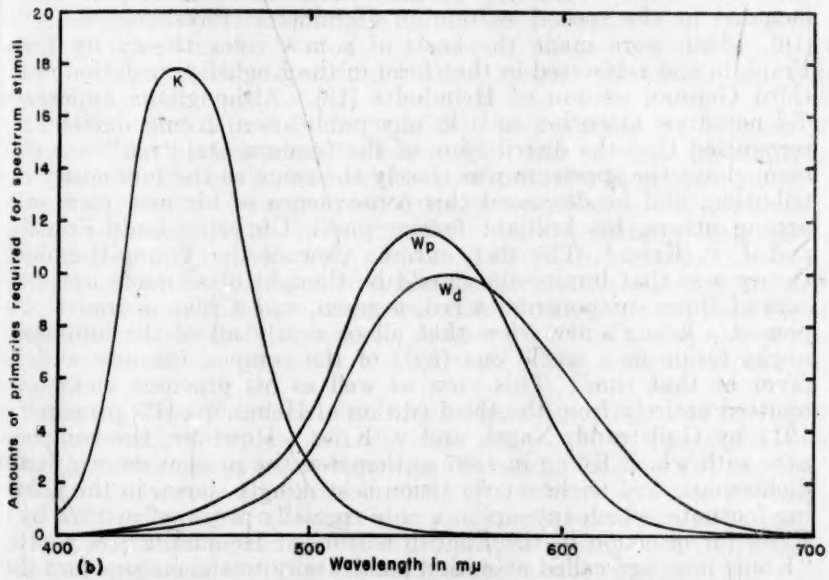


FIGURE 6.—*Comparison of the functions W_d, W_p, and K with the "fundamental-sensation" curves (dotted) derived by König in 1897.*

If allowance is made for the descending and expanding wavelength scale and for the energy distribution of gas light used by König, it will be noted that there is no essential difference between the two sets of functions.

In 1897, however, König published an important paper on tritanopia or "blueblindness", in which the choice of unitary blue as a "fundamental sensation" was given up. He says in a footnote [38, p. 716; 38a, p. 396], "I will immediately remark here that regarding the quality of this third fundamental sensation of the Young-Helmholtz color theory—whether it be blue or violet—I can still pass no definite judgment. In any case, however, I am now inclined to move it far closer to violet than was the case in the year 1886 (compare Sitz. Akad. Wiss. Berlin, July 29, 1886)."

As a result of this change in choice of third primary the "fundamental-sensation" curves bear a close resemblance to the functions W_d, W_p and K. Figure 6 (a) is a reproduction of König's figure 2 and is shown for comparison with figure 6 (b), which is a plot of the functions W_d, W_p, and K. The dotted curves of figure 6 (a) (the "fundamental-sensation" curves) are plotted against a descending and expanding wavelength scale, the curves are adjusted to equal area on this nonuniform scale and refer to the dispersion spectrum of gas light. Apart from these differences, however, it could be said that the functions W_d, W_p, and K are modern evaluations of the functions taken in 1897 by König to represent the "fundamental-sensation" curves of the eye. From the standpoint of the König theory, therefore, it is but to be expected that W_d and W_p taken together describe the color vision of a tritanope. It is no small tribute to König that the simplest representation of normal and dichromatic vision possible at the present time so closely resembles the picture given by him more than 40 years ago.

These later König views have so far received much less attention than his earlier evaluation of the "fundamental-sensation" curves included in the second edition of Helmholtz' Physiological Optics [16], which were made the basis of a new color theory by Ladd-Franklin and reinserted in that form in the English translation of the third German edition of Helmholtz [18]. Although he apparently did not draw attention to it in any publication, König immediately recognized that the distribution of the fundamental "red" sensation throughout the spectrum was closely the same as the luminosity distribution, and he discussed this consequence of his new view with, among others, his brilliant former pupil, Christine Ladd-Franklin, and J. v. Kries.[5] The then current view of the Young-Helmholtz theory was that luminosity should be thought of as made up of the sum of three components: a red, a green, and a blue or violet component. König's new view that all or nearly all of the luminosity might reside in a single one (red) of the components met with no favor at that time. This view as well as his previous views were omitted entirely from the third edition of Helmholtz [17] prepared in 1911 by Gullstrand, Nagel, and v. Kries. However, the completeness with which König in 1897 anticipated the present description of dichromatic and trichromatic vision is strikingly shown in the following footnote, which appears in a note specially prepared in 1924 by v. Kries for insertion in the English edition of Helmholtz [18, p. 412], "König long ago called attention incidentally to the curious fact that the luminosity values of the colours . . . . turn out to be very nearly the same function of the wave-length for deuteranopes and

[5] Communicated privately to the author by Ladd-Franklin in 1928.

persons with normal vision. Since in the case of deuteranopes light of long wave-lengths has no effect except on the red component, we must suppose also that this action depends on the wave-length in the same way. But then the further result is that the distribution of luminosity is not affected, or at least almost inappreciably affected, by the addition of the green component by which the deuteranopic visual organ is converted into a normal organ; in other words, that in the case of normal vision also the luminosity goes practically hand in hand with the action of the red component."

2. DOMINATOR-MODULATOR THEORY OF GRANIT

In 1943 Granit [12] gave a brief outline of a physiological theory of color perception based upon his oscillographic studies of the responses of isolated fibers from the optic nerves of animals (cat, guinea pig, frog, snake, rat). In the light-adapted eyes of these animals the simple spectral sensitivity curves recorded with his microelectrode technique were found to be of two types: (a) Broad absorption bands, called *dominators;* and (b) narrow bands, called *modulators.* The dominator of the light-adapted animal eye is found to have its maximum in the spectral region around 560 mμ. The form and spectral location of the dominator were found to be practically identical with the average curve obtained from massed receptors in the light-adapted eyes of the same species. This and its good correspondence with respect to form and location with the luminosity curve of the light-adapted human eye led Granit to the conclusion that the dominator is responsible for the sensation of brightness, which thus is taken as our dominant impression. Modulation of the dominant impression of brightness to color would seem to be the task of the much rarer modulators which occupy narrow bands of sensitivity in three preferential regions around 580 to 600 mμ, 520 to 540 mμ, and 450 to 470 mμ.

It will be noted from figure 6 (b) that the functions W_d, W_p, and K proposed here to represent dichromatic and normal trichromatic vision conform fairly well with the dominator-modulator theory. The K function is the narrowest of the three, and since it is unassociated with luminosity, could be thought of as a modulator for normal, protanopic, and deuteranopic vision. The W_p function is somewhat narrower than the W_d function and could be thought of as a modulator in the case of normal and tritanopic vision. The spectral location of these functions does not, however, conform perfectly with any of the three preferential regions found by Granit in his study of the eyes of animals.

Granit's view of deuteranopia differs somewhat from that suggested by the functions W_d and K. He says [12, p. 13], "Colour-blindness need not, but *can* be possible without parallel change of the photopic luminosity curve. A colour-blindness of this type would be the common form of red-green blindness known as deuteranopia, to be interpreted as absence of the 'red' and 'green' modulators, with the remaining dominator alone giving the normal luminosity curve." The view suggested by the functions W_d and K is that deuteranopia consists of the absence of only the green modulator, W_p.

Granit attacks the classical trichromatic theory of color blindness as follows [12, p. 14]: "The trichromatic theory regards white as due

to the summed effects of, chiefly, the 'red' and the 'green' sensitivity curves. This forces the theory to accept the consequence that removal of 'red' and/or 'green' should cause removal of the perception of luminosity in the same region of the spectrum. Hence there can be no colour-blindness without profound changes in the form and locus of the luminosity curve. It is an admission of failure to have to explain so important a phenomenon as deuteranopia by pushing it aside to be taken care of by the 'higher centres'." It is interesting to note that this criticism of classic three-components theory does not apply to the later König form of this theory.

It may be concluded that the functions W_d, W_p, and K are nearly, if not perfectly, consistent with Granit's dominator-modulator theory, and also that this theory was foreshadowed by König's later views. König, himself, however, began to be interested in the theoretical possibilities of an hypothetical post-receptor center of the visual mechanism apparently first suggested by Donders [5]. He states [38, p. 730; 38a, p. 414], "This is not the place to go into any further discussion of the hypothesis of the existence of a second more centrally located structure of the color system. I wish only to call special attention to the fact that with its assumption many difficulties still existing in the explanation of color vision in the extrafoveal and peripheral parts of the retina, for what I have called the blueblindness of the fovea, for the apparent achromaticity of sensations in the lowest brightness levels, and so forth, would be removed. Through assumption of pathological processes in this more centrally located color apparatus there could be explained further many cases of erythropsia, chloropia and so forth and finally perhaps color sense disturbances due to hysteria and so forth."

This view had been favored for some years by v. Kries [39, p. 269] and was adopted later by Adams [1] and Müller [47, 48]. Lest it appear that the concise account of dichromatic and normal trichromatic vision afforded by the functions W_d, W_p, and K establish the correctness of the three-components theory of vision according to König and Granit, and render further theorizing useless, two of the shortcomings of this form of three-components theory may be mentioned, and the way the zone theory of Müller overcomes these deficiencies may be indicated.

In the long-wave end stretch of the spectrum from 700 to 770 mμ the chromaticity is constant; that is, any part of this region of the spectrum can be matched perfectly for a normal observer by any other part, provided only that the luminances of the two be equalized. This constancy of chromaticity is indicated in the standard ICI coordinate system by the fact that X and Y bear the same ratio over this wavelength range, and the same thing is indicated from the functions W_d, W_p, and K from the fact that W_d and W_p also bear a constant ratio over the same range. If, as in König's later view, we regard W_d and W_p as the spectral distributions of the fundamental red and green sensations, the question may be asked, "What could account for the fact that while varying by a factor of 100 these two distributions still manage to bear exactly the same ratio?" There is only one answer at all plausible; the only way we would expect two processes to bear a constant ratio is that they are both functions of some other single process. Perhaps, for example, W_d and W_p are proportional to excitation of the fibers of the optic

nerve in the red and green sense, resulting from receptors (retinal cones, say) containing preponderantly a red-sensitive and a green-sensitive substance, respectively. If the green-sensitive substance were entirely insensitive for wavelengths greater than 700mμ, that is, suppose its sensitivity curve corresponded to W'_p (see fig. 4), the explanation for constant chromaticity for wavelengths longer than 700mμ would be very simple and believable; that is, only one photosensitive substance, the red sensitive, is affected by radiant energy of this wavelength range. The dependence of the fundamental red sensation upon this kind of radiant energy is customarily ascribed to leakage of a small fairly constant fraction of the green-sensitive substance into the predominantly red-sensitive cones. Thus it is seen that the functions W_d, W_p, and K, though they give a concise account of the connection between normal and dichromatic vision at the level of, perhaps, the fibers of the optic nerve, do not suffice to explain plausibly the constant chromaticity of the long-wave end stretch of the spectrum for the normal observer. To provide a satisfactory explanation, these functions have to be supplemented by another three-component system referring to the photosensitive substances themselves.

Although formulation of normal and dichromatic vision in terms of the functions W_d, W_p, and K gives a clear and satisfactory definition of the samples of radiant energy confused both by an average normal observer and average dichromatic observers, it does not provide any mechanism to explain the usual sensations. That is, these functions describe what the observers confuse but not what they see. Thus for the normal we have the fundamental sensations of red, green, and violet in equal amount summing to neutral. But when the red sensation is missing, as in protanopia, instead of having green and violet left, we find that blue and yellow are seen. Similarly when the green sensation is missing, as in deuteranopia or as in certain extra-foveal portions of the normal retina, blue and yellow are seen rather than red and violet, as might seem reasonable from the formulation of deuteranopia from W_d and K taken without W_p. And finally, when both green and violet are missing, neutral colors only are seen as in acquired total colorblindness, rather than the red which might be expected. This failure of the three-components theory to indicate correctly the sensations derivable from the various presumed combinations of the fundamental sensations has been pointed out innumerable times, chiefly by psychologists who could scarcely be expected to be satisfied with a formulation giving false implications of visual experience, even though it did predict correctly which samples of radiant energy are found to be identical in appearance. This failure led to the Hering and Ladd-Franklin theories of vision, and set König, Donders [5], and v. Kries to thinking about higher zones in the color apparatus. This lack is also felt by Granit, who remarks [12, p. 13], "The experiments with the cone-eye of the snake suggested that the dominator itself is composed of modulators joined together in such a fashion—either photochemically or by connections in the retinal synapses—as to operate as a *functional* unit. This assumption would explain why stimulation of all modulators together also causes an impression of white, and not of all colours confused. . . . Alternatively, the modulators could be coupled in antagonistic pairs which simultaneously neutralized each other at

the retinal or some higher level." The first suggestion accords closely with the Adams theory [1, 2], which is probably the first to follow explicitly the dominator-modulator form. The latter suggestion corresponds somewhat to the zone theory of Müller [47], which by 1924 had been elaborated so as to deal satisfactorily in a qualitative way with all known forms of dichromatic and monochromatic vision.

3. ZONE THEORY OF G. E. MÜLLER

The Müller theory includes three separate color systems, one in the zone of the initial photosensitive substances, a second in the zone of sensory retinal processes aroused by action of the initial photosensitive substances, and a third in the zone of excitations of optic-nerve fibers. The first color system has red, green, and violet primaries and accords with the classical Young-Helmholtz theory. The second system includes two pairs of antagonistic chromatic processes: Yellowishred-greenishblue (yR-gB), and greenishyellow-reddishblue (gY-rB). The first named of each pair has a lightening effect; the last named, a darkening effect. And, finally, the third system includes two pairs of antagonistic chromatic excitations and one nonantagonistic pair of achromatic excitations: Red-green (r-g), yellow-blue (y-b) and white-black (w-s). White does not cancel black, but combines with it to give gray.

Failure of the yR-gB process corresponds to protanopia. Yellowish red and greenish blue are the hues of the colors confused by the protanope with gray. Since the normal lightening effect of the yR-process is missing, the theory indicates that the luminosity function of the protanope is shifted toward the short-wave end, which corresponds to the facts.

Failure of the gY-rB process corresponds to tritanopia. Greenish yellow and reddish blue are the hues of the colors confused by the tritanope with gray. Since the normal lightening effect of the gY-process is missing, the theory indicates that the luminosity function of the tritanope is higher than normal at the short-wave end. The few data available [7, 8, 33, 34] are inconclusive concerning this indicated deviation from the normal luminosity function.

Failure of the r-g excitation corresponds to deuteranopia. Purplish red and green are the hues of the colors confused by the deuteranope with gray. The theory indicates that the deuteranopic luminosity function corresponds to the normal, which is the same indication given by the functions W_d, W_p, and K (see eq 11).

If, as seems likely, it is possible to quantify the Müller theory so as to make it embody the same dichromatic confusion colors as those indicated by the functions W_d, W_p, and K, a much more complete account of visual phenomena would be so achieved. The shortcomings of the König-Granit three-components theory outlined above would be overcome. One could then take his choice between a single color system yielding conveniently all of the dichromatic color confusions, or a three-system theory yielding the same confusions together with a prediction of dichromatic sensations.

The major theoretical point of difference between these two views lies in the account of deuteranopia. By the König-Granit theory, deuteranopia and protanopia are defects of similar character. By the Müller theory, deuteranopia is a defect of the optic-nerve fibers; protanopia and tritanopia, defects of the cones. Though there is no

conclusive evidence pointing to which, if either, view is correct, it may be significant, first, that diseases of the nerve-fiber layer of the retinal optic nerve and tract always produce the deuteranopic form of red-green blindness [33], never the protanopic form, and second, there have been several observers found who have tritanopia or protanopia in one eye [4, 19, 20, 21] and normal vision in the other, but never a case of congenital monocular deuteranopia [4, p. 78].

VIII. SUMMARY

There have been derived, chiefly from the work of Pitt, three functions of wavelength which permit easy definition of the samples of radiant energy found to be identical (metameric) not only by the ICI standard observer but also by the two most common types of red-green-blind observers, protanopes and deuteranopes. These three functions W_d, W_p, and K may be taken together to indicate the metamers of the normal observer; W_d and K, taken together indicate the metamers of the average deuteranopic observer; and W_p and K, those of the average protanopic observer. The functions W_d and W_p taken together also yield a close approximation to the less well determined metamers of the average tritanopic observer. Methods of using these functions to derive the variation in wavelength of neutral point for dichromatic observer with choice of neutral source are given, together with a convenient graphical solution of the ratio of protanopic reflectance to normal reflectance as a function of normal chromaticity. A derivation of the average protanopic, deuteranopic and tritanopic responses to the Farnsworth dichotomous test for color blindness is also given by way of these three functions. The functions W_d, W_p, and K, therefore, serve to make conveniently accessible the color confusions of dichromatic observers. These three functions also conform to the type of three-components color theory outlined in 1897 by Arthur König, and they are consistent with the dominator-modulator theory proposed by Granit in 1943. They do not, however, form the basis of a complete theory of vision such as that of Müller.

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WASHINGTON, July 25, 1944.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1619

Part of Journal of Research of the National Bureau of Standards, Volume 33, December 1944

SOME EXPERIMENTAL DATA ON THE HEATS OF COMBUSTION OF BENZOIC ACID AND CARBON (GRAPHITE)

By Edward J. Prosen and Frederick D. Rossini

ABSTRACT

Some experimental data are reported on the heats of combustion of benzoic acid and carbon (graphite). The data on benzoic acid support the change in the value for its heat of combustion recently reported from this Bureau by Jessup. The data on carbon (graphite) yield a slightly higher value for the heat of formation of carbon dioxide than that previously reported.

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I. INTRODUCTION

This paper presents some experimental data on the heats of combustion of benzoic acid and of carbon (graphite). The data on benzoic acid have already been referred to by Jessup [6][1] in his report on the new value for its heat of combustion. The data on carbon (graphite) are being utilized in the selection of a new best value for the heat of formation of carbon dioxide [9].

[1] Figures in brackets indicate the literature references at the end of the paper.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values reported in this paper are based is the international joule determined by the standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau [1].

The atomic weights of oxygen, hydrogen, and carbon were taken as 16.0000, 1.0080, and 12.010, respectively, from the 1941 table of International Atomic Weights [2].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [3].

Definitions of the symbols used are given in previous papers [4, 5].

III. METHOD

The method used in the present investigation is described in the report on the heats of combustion of the normal paraffin hydrocarbons [5].

IV. CHEMICAL APPARATUS, MATERIALS, AND PROCEDURE

1. SOURCE AND PURITY OF THE MATERIALS

The benzoic acid used in the combustion experiments of series I, II, III, IV, and V was NBS Standard Sample 39 e. The benzoic acid used in the experiments on calorimeter system *D* was NBS Standard Sample 39 f. These samples have been described previously by Jessup [6].

The samples of artificial graphite and Buckingham natural graphite were from the same source as those measured by Jessup [10]. The artificial graphite was of "spectrographic" grade [2] and was reported by the maker (National Carbon Co.) to contain less than 0.001 percent of ash. The Buckingham natural graphite was purified by alternate treatments with hydrochloric acid and hydrofluoric acid by H. B. Knowles, of this Bureau. The effect of various purification treatments has been reported by Jessup [10].

2. PREPARATION OF THE SAMPLES FOR COMBUSTION

The benzoic acid (about 1.51 g per experiment) was tightly pressed into a cylindrical pellet one-half inch in diameter in a pellet press. The benzoic acid was weighed in the platinum crucible (mass 8.2 g) in which it was burned.

The artificial graphite was burned in the form of a powder and the Buckingham natural graphite in the form of fine flakes. In each case, a sample of about 1.23 g was placed in a pile in the platinum crucible (mass 8.2 g), or in one of two platinum dishes (mass 1.6 g or 0.7 g) in which it was burned.

[2] See the spectrochemical analysis of another sample of this material reported by B. F. Scribner, of this Bureau, in table 5 of reference [10].

3. IGNITION OF THE SAMPLES

The samples were ignited in the bomb by a coil of 5 cm of Parr wire placed about 1 mm above the sample in the platinum crucible or dish [4].

4. PURIFICATION OF THE OXYGEN

The oxygen for combustion was purified as described previously [4].

5. EXAMINATION OF THE PRODUCTS OF COMBUSTION

The products of combustion were examined as previously described [4]. No products of incomplete combustion were detected in the gaseous products from any of the experiments with benzoic acid or with graphite. In the experiments with graphite, a small amount (several milligrams) of the sample remained unburned.

6. DETERMINATION OF THE AMOUNT OF REACTION

For the combustion experiments on graphite, the amount of reaction was determined from the mass of carbon dioxide formed, with 44.010 g of carbon dioxide being taken as equivalent to 1 mole of carbon.

For the experiments on benzoic acid, the amount of reaction was determined from the mass of benzoic acid placed in the bomb, for the purpose of better comparison with the results of Jessup [6]. In addition, as a further check on the purity of the chemical reaction occurring in the combustion experiment, measurements of the carbon dioxide formed in the combustion in the bomb were made in two series of experiments with benzoic acid. The results of these measurements, giving the ratio of the mass of carbon dioxide formed to the amount of carbon dioxide calculated stoichiometrically from the mass of sample, are as follows:

Series	Number of experiments	Average ratio	Standard deviation of the mean
(1)	6	0.999954	±0.000080
(2)	4	.999987	±.000081

V. CALORIMETRIC APPARATUS AND PROCEDURE

1. APPARATUS

The apparatus used in this work was the same as that described in references [4] and [5]. The calorimeter systems *A*, *B*, and *C* referred to in this report are identical with those described in reference [5]. For the later experiments on graphite, calorimeter system *D* was used, which differed from calorimeter system *C* only in the calorimeter heater. The latter consisted of a heating element of about 150 ohms of manganin wire (No. 30 AWG) spiraled inside a copper tube one-quarter inch in diameter and 6 feet long, with magnesia insulation. This heater turned out to be unsatisfactory for use in precise experiments with electric energy because the electrical insulation was not good enough, and it was therefore used only to bring the calorimeter

system to the proper starting temperature. On this account, the energy equivalent of calorimeter system D had to be determined in terms of that of calorimeter system C by the use of benzoic acid to obtain the ratio of the two energy equivalents.

2. DETERMINATION OF THE IGNITION ENERGY

The ignition energy was determined as described in reference [4].

3. CORRECTION FOR THE FORMATION OF NITRIC ACID

The correction for the nitric acid formed in the reaction in the bomb was made as described previously [4, 5].

4. ELECTRIC-ENERGY EQUIVALENT

The experiments made to determine the electric-energy equivalent of calorimeter systems A, B, and C are described in detail in reference [5]. The energy equivalent of calorimeter system D was determined in terms of that of calorimeter system C by the use of benzoic acid (NBS Standard Sample 39 e with calorimeter system C and NBS Standard Sample 39 f with calorimeter system D) to obtain the ratio of the two energy equivalents. These two samples of purified benzoic acid were essentially identical in purity, and Jessup found no significant difference in their heats of combustion [6].

5. COMBUSTION EXPERIMENTS

The procedure followed in performing the calorimetric combustion experiments is described in detail on pages 302 and 303 of reference [4].

VI. RESULTS OF THE PRESENT INVESTIGATION

1. ELECTRIC-ENERGY EQUIVALENT

The electric-energy equivalents of calorimeter systems A, B, and C are given in reference [5]. The results of the experiments to determine the energy equivalent of calorimeter system D through its ratio to that of calorimeter system C, by the use of benzoic acid, are given in table 1. For convenience and clarity in presentation, the data are all reported in terms of the energy equivalent of calorimeter system C, and the following relations were used for the ratios of the energy equivalents of the several systems:

$$E_s\,(C) = 137717.4 \pm 13.9 \text{ int. j/ohm.}$$
$$E_s\,(A) = 0.998955\ E_s\,(C) = 137573.5 \pm 16.2 \text{ int. j/ohm.}$$
$$E_s\,(B) = 1.002003\ E_s\,(C) = 137993.3 \pm 14.6 \text{ int. j/ohm.}$$
$$E_s\,(D) = 0.991085\ E_s\,(C) = 136489.6 \pm 14.5 \text{ int. j/ohm.}$$

TABLE 1.—*Energy equivalent of calorimeter system D*

Experiment number	Mass of benzoic acid [a]	k	K	U	ΔR_c	Δr_i	Δr_n	B'	Deviation from mean
	g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g of benzoic acid*	*Ohm/g of benzoic acid*
1	1.51973	0.002005	0.000934	0.000474	0.294674	0.000409	0.000045	0.1936238	0.0000091
2	1.52023	.001973	0.00860	.000446	.294770	.000416	.000051	.1936147	.0000000
3	1.50071	.001967	.001014	.000480	.290981	.000418	.000047	.1936084	−.0000063
4	1.53028	.001972	.000856	.000432	.296711	.000414	.000053	.1936119	−.0000028
Mean								0.1936147	
Standard deviation of the mean								±.0000033	

[a] NBS Standard Sample 39f.

2. COMBUSTION EXPERIMENTS

The results of five series of experiments on the combustion of benzoic acid are given in table 2, in which the symbols have the same meaning as before [4, 5], except that B' is the corrected rise in temperature of the standard calorimeter system, expressed in ohms on the given platinum resistance thermometer, divided by the mass of benzoic acid.

TABLE 2.—*Combustion experiments on benzoic acid*

Series number	Number of experiments [a]			Mass of benzoic acid [b]	k	K	U	ΔR_c	Δr_i	Δr_n	B'	
	A	B	C								Mean	Standard deviation of mean
				g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g benzoic acid*	*Ohm/g benzoic acid*
I	5			1.51447 to 1.51505	0.001927 to .001937	0.000993 to .001040	0.000098 to .000114	0.291335 to .291476	0.000406 to .000426	0.000023 to .000027	0.1918961	±0.0000088
II		6		1.50186 to 1.51581	.001940 to .001951	.001060 to .001151	.000074 to .000125	.288031 to .290703	.000408 to .000420	.000063 to .000072	.1919072	±.0000157
III		4		1.51470 to 1.51800	.001934 to .001946	.000782 to .001224	.000530 to .000565	.290615 to .291283	.000393 to .000414	.000064 to .000076	.1918792	±.0000215
IV		4		1.51796 to 1.51873	.001928 to .001938	.000806 to .001244	.000179 to .000195	.291165 to .291391	.000409 to .000415	.000074 to .000079	.1918608	±.0000190
V			5	1.49749 to 1.52035	.001944 to .001954	.001224 to .001345	.000275 to .000349	.287718 to .292072	.000403 to .000418	.000013 to .000013	.1918857	±.0000109
Weighted mean											0.1918886	

[a] The numbers in columns A, B, and C indicate the number of experiments performed with calorimeter systems A, B, C, respectively (see section V-1).
[b] NBS Standard Sample 39 e.

The results of the four series of experiments on the combustion of Buckingham natural graphite and artificial graphite are given in table 3.

TABLE 3.—*Combustion experiments on graphite*

Substance	Series number	Number of experiments[a]		Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_e	B	
		C	D								Mean	Standard deviation of mean
				g	min^{-1}	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g* CO_2	*Ohm/g* CO_2
Buckingham natural graphite	I	5		4.50052 to 4.53086	0.001942 to .001958	0.001273 to .001428	0.000300 to .000342	0.292856 to .293272	0.000379 to .000409	0.000002 to .000002	0.0649887	±0.0000029
	II		4	4.30513 to 4.58939	.002017 to .001970	.000449 to .001072	.000430 to .000474	.282664 to .301402	.000393 to .000416	.000008 to .000013	.0649927	±.0000076
Artificial graphite	I	5		4.50375 to 4.52566	.001960 to .001962	.001042 to .001315	.000308 to .000376	.293214 to .294588	.000405 to .000417	.000002 to .000003	.0649972	±.0000050
	II		3	4.49369 to 4.51621	.001976 to .001988	.000724 to .001071	.000378 to .000456	.293225 to .296666	.000409 to .000419	.000024 to .000041	.0649997	±.0000124
Weighted mean											0.0649920	

[a] The numbers in columns C and D indicate the number of experiments performed with calorimeter systems C and D, respectively (see section V-1).

As stated in the preceding section, all the foregoing values of B and B' are expressed in terms of the energy equivalent of system C.

3. VALUES OF THE HEATS OF COMBUSTION

The value of the heat evolved in the combustion of benzoic acid under the conditions of the bomb process, for 28° C, is the product of the mean value of B' (from table 2) and of E_s (C), the energy equivalent of calorimeter system C:

$$Q'_B(28° \text{ C}) = 26426.4 \pm 2.2 \text{ int. j/g.}$$

Conversion to 25° C, and the standard conditions of the bomb process [11], by the use of the relation given in footnote 6, page 261, of reference [6], yields

$$Q_B(25° \text{ C}) = 26429.3 \pm 2.2 \text{ int. j/g.}$$

The value of the heat of combustion of graphite in the bomb process is the product of the mean value of B (table 3), the energy equivalent of calorimeter system C, and the molecular weight of carbon dioxide [5]:

$$-\Delta U_B(28° \text{ C}) = 393913 \pm 55 \text{ int. j/mole.}$$

Conversion to $-\Delta Hc°$ at 25° C, which is the decrement in heat content with both reactants and the product in their thermo-dynamic reference states, yields

$$-\Delta Hc° \ (25° \text{ C}) = 393502 \pm 55 \text{ int. j/mole.}$$

The conversion to $-\Delta Hc°$ at 25° C involves -409 j/mole in the Washburn correction [11], $+1$ j/mole for $P\Delta V$, and -3 j/mole for the change from 28° to 25° C.

The over-all uncertainty assigned to each final value above was taken as the square root of the sum of the squares of the following components, as appropriate: (a) Twice the standard deviation of the mean of the series of combustion experiments; (b) an uncertainty of 0.010 percent in the determination of the absolute value of the amount of reaction; (c) twice the standard deviation of the mean (or weighted mean) of the series of experiments to determine the energy equivalent; and (d) an uncertainty of 0.010 percent in the determination of the absolute value of the electric energy.

VII. DISCUSSION

The value for the heat of combustion of benzoic acid obtained in this investigation is in complete accord with that reported recently from this Bureau by Jessup [6], the difference being 0.003 ± 0.013 percent.

The value for the heat of combustion of graphite given here is slightly higher than that previously reported, and the data are being used in another report [9], in conjunction with a recalculation of the data previously reported [10, 12, 13], to obtain a selected "best" value for the heat of formation of carbon dioxide.

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WASHINGTON, August 15, 1944.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1620

Part of Journal of Research of the National Bureau of Standards, Volume 33, December 1944

HEAT OF FORMATION OF CARBON DIOXIDE AND OF THE TRANSITION OF GRAPHITE INTO DIAMOND

By Edward J. Prosen, Ralph S. Jessup, and Frederick D. Rossini

ABSTRACT

A recalculation of data previously reported on the heats of combustion of graphite and diamond, together with consideration of some new data on graphite, yielded the following selected "best" values for the heats of combustion of graphite and diamond and of the transition of graphite into diamond:

C (c, graphite) + O_2 (gas) = CO_2 (gas); $\Delta H^\circ_{298.16} = -393{,}447 \pm 45$ int. j/mole = $-94{,}051.8 \pm 10.8$ cal/mole

C (c, diamond) + O_2 (gas) = CO_2 (gas); $\Delta H^\circ_{298.16} = -395{,}343 \pm 96$ int. j/mole = $-94{,}505.1 \pm 22.9$ cal/mole.

C (c, graphite) = C (c, diamond); $\Delta H^\circ_{298.16} = 1896 \pm 85$ int. j/mole = 453.2 ± 20.3 cal/mole.

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I. INTRODUCTION

As a result of a recalculation of the data previously reported on the heats of combustion of graphite and diamond [1, 2, 3],[1] together with consideration of some new data on graphite [4], revised "best" values have been obtained for the heat of formation of carbon dioxide and for the heat of transition of graphite into diamond.[2]

II. RECALCULATION OF THE DATA OF DEWEY AND HARPER ON GRAPHITE

For the reaction

$$C\ (c,\ graphite) + O_2\ (gas) = CO_2\ (gas) \qquad (1)$$

the data of Dewey and Harper [1] previously yielded [3] the value

$$\Delta H^\circ_{298.16} = -393{,}317 \pm 110 \text{ int. j/mole.} \qquad (2)$$

This value was based on the 1934 NBS value for the heat of combustion of benzoic acid [5], which was used by Dewey and Harper for

[1] Figures in brackets indicate the literature reference at the end of this paper.

[2] Revised values for the corresponding free energies are given in another report [10].

determining the energy equivalent of their calorimeter. The conversion of their data to the new 1942 value for the heat of combustion of benzoic acid [6] requires a correction of +0.0336 percent, following the procedure described on page 262 of reference [6]. On the new basis, the data of Dewey and Harper [1] yield for reaction (1)

$$\Delta H^{\circ}_{298.16} = -393{,}449 \pm 100 \text{ int. j/mole.} \quad (3)$$

III. RECALCULATION OF THE DATA OF JESSUP ON GRAPHITE

For reaction (1), the data of Jessup [2] previously yielded

$$\Delta H^{\circ}_{298.16} = -393{,}363 \pm 51 \text{ int. j/mole.} \quad (4)$$

The values originally reported by Jessup [2] from his experiments on the *B* calorimeter system were based solely on a value of the energy equivalent determined with electrical energy, although a determination of the energy equivalent of this system was also made with benzoic acid. In the present recalculation of Jessup's data, the reported results of the benzoic acid calibration have been converted to the new value for benzoic acid [6], and combined with the results of the electrical calibration by weighting the two mean values of energy equivalent inversely as the squares of their assigned uncertainties.[3] The value obtained in this way for the energy equivalent of Jessup's *B* calorimeter system is higher by 0.0038 percent than that originally reported. The values originally reported by Jessup [2] from his experiments on the *C* calorimeter system were based on calibration experiments performed with benzoic acid. Conversion to the new value for benzoic acid according to the prescribed procedure [6] requires a correction of +0.0107 percent. The effect of applying the above corrections to the values reported by Jessup for the energy equivalents of his *B* and *C* calorimeter system is to raise his value for the heat of reaction (1) by 0.0071 percent, so that his finally recalculated result for this reaction becomes:

$$\Delta H^{\circ}_{298.16} = -393{,}391 \pm 55 \text{ int. j/mole.} \quad (5)$$

IV. SUMMARY OF THE DATA ON GRAPHITE

Including the new data reported by Prosen and Rossini [4], which are based on measurements with electric energy, the values (and assigned uncertainties [7]) for the heat of reaction (1) are as follows:

From	$\Delta H^{\circ}_{298.16}$
Dewey and Harper [1]	−393,449 ±100 int. j/mole.
Jessup [2]	−393,391 ±55 int. j/mole.
Prosen and Rossini	−393,502 ±55 int. j/mole.

[3] The term assigned uncertainty as used here denotes $\sqrt{d^2+a^2}$, where *d* is twice the standard deviation of the mean calculated from the deviations of individual results from the mean value of energy equivalent, and *a* is an allowance of 0.010 percent for errors in electrical measuring instruments in the case of an electrical calibration, or for error in the value used for the heat of combustion of benzoic acid in the case of a calibration with this substance.

Weighting these values inversely as the squares of their assigned uncertainties,[4] there is obtained for reaction (1)

$$\Delta H^{\circ}_{298\cdot16} = -393{,}447 \pm 45 \text{ int. j/mole.} \quad (6)$$

Using the factor 1/4.1833 [9], this becomes

$$\Delta H^{\circ}_{298\cdot16} = -94{,}051.8 \pm 10.8 \text{ cal/mole.} \quad (7)$$

V. HEAT OF TRANSITION OF GRAPHITE INTO DIAMOND

The present "best" value for the heat of transition of graphite into diamond may be obtained from the experiments performed by Jessup [2], in which the same calorimeter system was used for both graphite and diamond (macrocrystalline). By treating the data essentially as described by Prosen and Rossini in the determination of the heats of isomerization of the hexanes [8], there is obtained from Jessup's data on the *C* calorimeter system the following value for the ratio of the heat evolved, per gram of carbon dioxide formed, in the combustion of diamond to that in the combustion of graphite: 1.004820 ± 0.000216. With the value for the heat of combustion of graphite given by eq 6, there is obtained for

$$\text{C (c, diamond)} + O_2 \text{ (gas)} = CO_2 \text{ (gas)}; \ \Delta H^{\circ}_{298\cdot16} = -395{,}343 \pm 96 \textit{ int. j/mole} = -94{,}505.1 \pm 22.9 \textit{ cal/mole}, \quad (8)$$

and for

$$\text{C (c, graphite)} = \text{C (c, diamond)}; \ \Delta H^{\circ}_{298\cdot16} = 1896 \pm 85 \textit{ int. j/mole} = 453.2 \pm 20.3 \textit{ cal/mole}. \quad (9)$$

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[1] P. H. Dewey and D. R. Harper, 3d, J. Research NBS **21,** 457 (1938) RP1139.
[2] R. S. Jessup, J. Research NBS **21,** 491 (1938) RP 1140.
[3] F. D. Rossini and R. S. Jessup, J. Research NBS **21,** 491 (1938) RP1141.
[4] E. J. Prosen and F. D. Rossini, J. Research NBS **33,** 439 (1944) RP 1619.
[5] R. S. Jessup and C. B. Green, J. Research NBS **13,** 469 (1934) RP721.
[6] R. S. Jessup, J. Research NBS **29,** 247 (1942) RP1499.
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[9] E. F. Mueller and F. D. Rossini, Am. J. Phys. **12,** 1 (1944).
[10] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D Rossini, National Bureau of Standards. Unpublished.

WASHINGTON, August 16, 1944.

[4] The resulting uncertainty of the weighted mean [7] becomes ±36 j/mole, but has been arbitrarily increased to ±45 j/mole.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1621

Part of Journal of Research of the National Bureau of Standards, Volume 33, December 1944

PREPARING REFRACTORY OXIDES, SILICATES, AND CERAMIC MATERIALS FOR ANALYSIS, BY HEATING WITH ACIDS IN SEALED TUBES AT ELEVATED TEMPERATURES

By

Edward Wichers, William G. Schlecht, and Charles L. Gordon

ABSTRACT

This paper describes the preparation for analysis of a number of refractory oxides, ceramic materials, and minerals by decomposition with hydrochloric or hydriodic acid at temperatures up to 300° C. All the oxides of the elements in the second, third, and fourth groups of the periodic system, with the exception of silica, titania, zirconia, and possibly hafnia, respond to the treatment. A number of silicate minerals, ordinarily difficult to prepare for analysis, are likewise successfully decomposed.

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I. INTRODUCTION

The work already reported on the preparation of refractory platiniferous materials for analysis [1] led naturally to trials of a similar procedure for attacking various minerals and ceramic materials that are difficult to decompose by the analyst's customary methods. Jannasch [2] used such a method some 50 years ago. He treated refractory silicate rocks with hydrochloric acid in sealed tubes at temperatures up to 400° C. To prevent contaminating the solutions with silica and other constituents of the glass, he placed the samples in loosely stoppered platinum capsules inside the sealed glass tubes, with acid both inside and outside the capsules. If air was not displaced from the tube before it was sealed, considerable platinum dissolved. Jannasch's method apparently has not come into general use, but the procedure seems worthy of further consideration, especially

[1] E. Wichers, W. G. Schlecht, and C. L. Gordon, *Attack of refractory platiniferous materials by acid mixtures at elevated temperatures*, J. Research NBS **33**, 363 (1944) RP1614.

[2] P. Jannasch, Ber. deut. chem. Ges. **24**, 273 (1891); Z. anorg. Chem. **6**, 72 (1894).

since modern laboratory glass is so little attacked by hydrochloric acid at high temperatures.

The equipment used in the trials here reported was the same as that described for dissolving iridium and its alloys, and is described in detail in a third paper.[3] In many instances samples weighing 0.1 g were used. These were treated with 1 ml of hydrochloric acid (36 weight-percent HCl) in 4- by 8-mm tubes, about 20 cm long. These tubes required no external protection. Larger samples were treated in tubes of suitable size (up to 15-mm bore). In these larger tubes the internal pressure developed during treatment of the sample was compensated for by external pressure of carbon dioxide within a steel container.

II. TREATMENT WITH HYDROCHLORIC ACID

1. ALUMINUM OXIDE, CLAY, AND SILICEOUS MATERIALS HIGH IN ALUMINA

One of the first materials to be tried was sintered aluminum oxide, which had to be examined for a minute content of sulfate (about 0.01 percent). Ignited alumina is, of course, wholly unattacked by hydrochloric acid at temperatures attainable in open vessels. Even at 160° C there was no visible attack in 4 hours, but at 260° C the material was brought completely into solution within 15 hours with a quantity of hydrochloric acid only 10 percent in excess of the stoichiometric requirement. The resulting solution was a nearly ideal one in which to determine sulfate by means of precipitation with barium chloride. The alternative procedure of fusing the samples with sodium carbonate or with borax not only might have introduced sulfur compounds in amounts as large as those in the sample, but would have yielded a solution containing an undesirable amount of alkali salts.

Later a 2-g sample of fused aluminum oxide in the form of a 60-mesh powder was completely dissolved in 20 ml of hydrochloric acid in 35 hours at 300° C. Burnt alumina refractories (NBS Standard Samples 76 and 78) were completely decomposed by treatment at 300° C for 24 hours. In these and most of the other trials no attempt was made to determine the optimum conditions of treatment but only to find out whether the method appeared to be useful for a considerable variety of materials. In the course of these trials there was occasion to prepare for analyses a considerable number of porcelains containing 36 to 97 percent of alumina and up to 57 percent of silica. All of these were successfully decomposed at 300° C.

2. OTHER REFRACTORY OXIDES

Beryllium oxide that had been ignited at 1,500° C was completely dissolved within 16 hours at 250° C. Bolivian tin ore, largely cassiterite, was incompletely attacked at 200° C but completely decomposed in 24 hours at 250 ° C. Ceric oxide was completely at-

[3] C. L. Gordon, W. G. Schlecht, and E. Wichers, *Use of sealed tubes for the preparation of acid solutions of samples for analysis, or for small scale refining: Pressures of acids heated above 100° C*, J. Research NBS 33, 457 (1944) RP1622.

tacked at 300° C in 18 hours, and equally well when nitric acid was used instead of hydrochloric acid. Nitric acid was found to attack fused alumina only slightly in 72 hours at 300° C. Titanium and zirconium oxides showed no sign of attack by concentrated hydrochloric acid in 18 hours at 300° C. Raising the temperature to 350° C resulted in a slight attack of the zirconia in a 4-hour period. A slight attack was also accomplished at 250° C with specially fortified hydrochloric acid (75 weight-percent of HCl) in a 16-hour period. Neither variation resulted in significant attack of titanium oxide. In view of the resistance of zirconium oxide to hydrochloric acid, it was of special interest to find that a ceramic material containing about 50 percent of zirconia and 35 percent of silica could be successfully decomposed for analysis. This was also done with a special ceramic material containing 10 percent of zirconia, 80 percent of thorium oxide, and 10 percent of yttrium oxide.

3. MINERALS

In studying the attack of various minerals, weighed samples of approximately 0.1 g were treated with 1 ml of acid for 48 hours at 300° C. When the tubes were opened the undissolved residue was collected on filter paper, washed, and ignited. It was then treated with hydrofluoric and sulfuric acids to volatilize the silica. The difference between the weight of sample taken and the weight of the residue after this treatment was taken as a measure of the degree of completeness of the attack. The following minerals were found to be completely attacked, or substantially so in the sense that the weight of residue was less than 1 percent of the weight of the sample taken: Muscovite, amphibole, Ab_3An_{97} (anorthite), tourmaline, clinochlore, cordierite (iolite), sillimanite, spinel, and chromite. A number of others left residues not exceeding about 5 percent of the sample weight and were classified as nearly completely attacked. They were $Ab_{52}An_{48}$ (andesine), talc, diaspore, allanite, $Ab_{20}An_{80}$ (bytownite), allmandite garnet, and sphene (titanite). It seems not unlikely that some variation in the treatment of these specimens would have resulted in complete attack. Beryl, topaz, orthoclase, samarskite, and dumortierite were partially decomposed by the treatment described, whereas $Ab_{63}An_{37}$ (andesine), $Ab_{96}An_4$ (albite), and $Ab_{80}An_{20}$ (oligoclase) were virtually unattacked.

The albite-anorthite series of minerals was of special interest because the degree of attack ranged from none for albite to complete for anorthite. These minerals responded as shown in table 1. The refractive indices of most of these minerals were determined by C. P. Saylor of this Bureau. The compositions of these minerals were then obtained from the relation between the refractive index and the albite to anorthite ratio.[4] The relation between the attack by hydrochloric acid and the silica content of the mineral plotted as a function of the composition is shown in figure 1.

[4] E. S. Larsen and H. Berman, The Microscopic Determination of the Nonopaque Minerals [2d ed.] Bul. 848, U. S. Geological Survey.

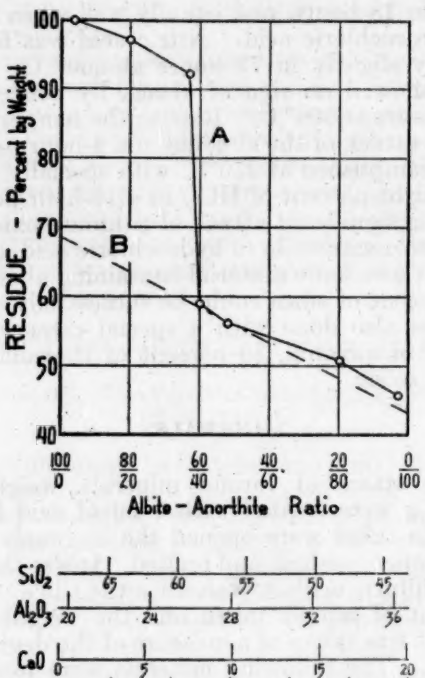

FIGURE 1.—*Decomposition of the albite-anorthite series of plagioclase feldspars by hydrochloric acid at 300° C.*

A, percentage by weight of mineral undissolved after 48 hours; *B*, percentage by weight of silica in the mineral (theoretical).

TABLE 1.—*Degree of attack of the albite-anorthite series of plagioclase feldspars*

Mineral [4]	Composition by weight [1]				Percentage of sample undissolved [2]	Percentage of sample lost by HF treatment [3]
	SiO_2	Al_2O_3	CaO	Na_2O		
	%	%	%	%		
$Ab_{96}An_4$	68	20	1	11	100.0	39.8
$Ab_{90}An_{10}$	64	23	4	9	97.1	32.9
$Ab_{83}An_{17}$	59	26	7	7	92.3	50.2
$Ab_{80}An_{20}$	58	26	8	7	59.0	56.6
$Ab_{73}An_{27}$	56	28	10	6	56.1	50.1
$Ab_{50}An_{50}$	48	33	16	2	50.8	49.1
Ab_3An_{97}	44	36	20	0	45.7	44.5

[1] From index measurements by C. P. Saylor.
[2] Undissolved residue after filtration of the contents of the sealed tube and ignition of the paper.
[3] Determined by treatment of the residue with hydrofluoric acid and sulfuric acid, followed by ignition to oxides.
[4] Ab=albite; An=anorthite.

4. ROCKS

Two rocks, reddish andesite and rhyolite, were also tried. They were partially attacked and no difference was found in the degree of attack in periods of 2 and 3 days at 300° C. Apparently, certain constituents of these rocks were rather readily decomposed, whereas others remained unattacked. The difference in this respect between such minerals as mica and the feldspars suggests that the treatment might be useful in determining the amounts of these minerals in granites.

Bauxite (NBS Standard Sample 69) was completely attacked.

III. TREATMENT WITH HYDRIODIC ACID

Caley and Burford [5] used hydriodic acid for the solution of some difficultly soluble compounds. They noted that the alkaline earth sulfates are not decomposed by cold hydriodic acid but decompose at higher temperatures. Trials with the sealed 2-ml tubes containing 1 ml of hydriodic acid (56 weight-percent of HI) and 0.100 g of material were made at 300° C for 48 hours. Barium sulfate was found to be completely decomposed, as was fused alumina (60 mesh). Sillimanite and anorthite were nearly completely attacked, but andesine, orthoclase, oligoclase, and zirconia were unattacked, as compared with slight attack by hydrochloric acid. It was found in the case of the minerals that the attack by hydriodic acid (56 weight-percent of HI) was in general slightly less than by hydrochloric acid (36 weight-percent of HCl) at the same temperature.

IV. CONTAMINATION OF THE SAMPLE BY DISSOLVED OXIDES FROM THE SEALED TUBE

The attack of Pyrex glass under the conditions described is small enough to cause no concern in making many types of analyses. The principal constituents of Pyrex laboratory glass are the oxides of silicon, boron, aluminum and sodium. In careful analytical work the removal of these constituents from the glass must be taken into account. The magnitude of the attack is illustrated by a "blank" experiment in which 5 ml of hydrochloric acid (36 weight-percent of HCl) was heated at 300° C for 24 hours. The resulting solution was rinsed into a platinum crucible, evaporated, and the residue dried at 100° C. After treatment with sulfuric acid and ignition, it weighed 0.0032 g, of which 0.0018 g was lost by treatment with hydrofluoric and sulfuric acids in the usual manner. The tube had an internal surface area of 12 cm^2, hence the amount of material removed from the glass, as weighed after treatment with sulfuric acid and ignition, was 0.00026 g/cm^2.

For work in which the degree of attack on the glass is excessive, recourse can be had to Jannasch's device of capsules of platinum within the sealed glass tubes. This involves the disadvantage of keep-

[5] E. R. Caley and M. G. Burford, Ind. Eng. Chem., Anal. Ed. 8, 63-7 (1936).

ing the tubes upright, with a consequent slower rate of attack than when the sample can be distributed along the length of the tube. An alternative method is to use a platinum-lined pressure vessel of steel. To avoid the attack of platinum that Jannasch observed, the air in the tube can be displaced with some inert gas or, more simply, a small amount of sulfur dioxide can be added to the hydrochloric acid. A number of trials showed that the optimum concentration of sulfur dioxide for this purpose is 0.0013 g/ml of acid. Smaller amounts failed to protect the platinum completely, and larger amounts resulted in the deposition of sulfur.

WASHINGTON, May 25, 1944.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1622

Part of Journal of Research of the National Bureau of Standards, Volume 33, December 1944

USE OF SEALED TUBES FOR THE PREPARATION OF ACID SOLUTIONS OF SAMPLES FOR ANALYSIS, OR FOR SMALL-SCALE REFINING: PRESSURES OF ACIDS HEATED ABOVE 100° C

By Charles L. Gordon, William G. Schlecht, and Edward Wichers

ABSTRACT

This paper describes special technics suitable for the use of sealed tubes in treating refractory materials with hydrochloric acid and other acid mixtures at elevated temperatures. Methods for filling, for sealing, and for opening tubes are discussed. The feasibility of reuse of tubes of Pyrex glass is discussed with some observed phenomena of the attack of the glass by the acids. A protecting shell is described together with a method of using solid carbon dioxide to provide the compensating pressures needed to protect the sealed tubes from bursting. The pressures developed on heating hydrochloric acid and mixtures of hydrochloric acid with nitric or perchloric acids were measured in a special gage, which is described.

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I. INTRODUCTION

The work already reported [1] [2] on the preparation of refractory materials for analysis involved the technics of the sealed tube, and because of the high pressures encountered, methods for the protection of these tubes against explosions were devised. The pressures developed by the acids used were so great that the tubes, with the exception of those of rather small bore, required protection by an external compensatory pressure.

For the larger-scale solution of refractory materials a heavy-walled 15-by 20-mm Pyrex tube was used and provided with a filling stem of 4-by 8-mm Pyrex tubing, as shown in figure 1. The technic of filling these tubes through the 4-by 8-mm stems and subsequently sealing

[1] E. Wichers, W. G. Schlecht, and C. L. Gordon, *Attack of refractory platiniferous materials by acid mixtures at elevated temperatures*, J. Research NBS **33**, 363 (1944) RP1614.

[2] E. Wichers, W. G. Schlecht, and C. L. Gordon, *Preparing refractory oxides, silicates, and ceramic materials, for analysis, by heating with acids in sealed tubes at elevated temperatures*, J. Research NBS **33**, 451 (1944) RP1621.

them is the same as for the 4-by 8-mm experimental tubes used in studying reaction rates.

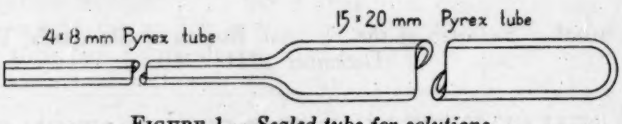

FIGURE 1.—*Sealed tube for solutions.*

The volume of the main tube is approximately 1.77 ml/cm. The tube is made twice the length that will accommodate the desired amount of reacting mixture.

II. CHARGING, SEALING, AND OPENING THE TUBES

In charging the tubes, the weighed sample is first introduced through the open end or through the stem. If the pieces of the the sample are too large to go through the neck, they should be broken up. If this fails, they must be put into the larger tube before the stem is sealed on. The seal of the stem to the larger tube must always be carefully annealed to avoid excessive strains at this point. If the tube is to be charged with hydrochloric acid, especially if fortified acid is used, it should be cooled in ice. The oxidizing agent, if used, is added next. If this is sodium chlorate, the tube must be chilled enough to freeze the hydrochloric acid and to keep it frozen until the sealing is completed. Sealing may be done by constricting and drawing off a short piece of the tube (or stem) and then working down the sealed tip in the usual way. It can also be done by allowing the open end of the stem to flow together by heating with an oxygen-gas flame and then warming the tube enough to blow out the end to a rounded shape. Good seals made in this way are easier to make and also are stronger than the drawn out seal, unless the latter type of seal is reworked to a hemispherical shape. In either case, care must be taken to be certain that a minute capillary opening is not left, otherwise the gas used to provide the compensating pressure may enter the tube during the heating but be prevented from escaping if the minute orifice is plugged by reaction products. This will leave a dangerously high pressure in the tube when the compensating pressure is released, which is likely to shatter the tube when it is subsequently cut open.[3]

The tube should be placed in the oven horizontally after tipping it to distribute the sample along most of its length.

When the reaction period is completed, the tube can be placed with its lower end in a beaker of warm water. Vapors condensing in the upper end soon wash the glass free of solution. Before opening the tube it is usually best to chill it in a freezing mixture or in solid carbon dioxide. This condenses residual chlorine and diminishes the pressure of nitrogen, which will be present if nitric acid is used as the oxidizing agent. If volatile reaction products are present, chilling the tube before it is opened serves to prevent their escape. When the tube is well chilled the end is cut open, whereupon the tube is inverted in a beaker containing water or whatever liquid may be chosen to dilute

[3] Any type seal can be tested for a capillary leakage by standing the carefully wiped tube upside down over a small piece of litmus paper. If the acid mixture is hydrochloric acid with nitric acid, sodium chlorate, or other oxidant that reacts with the hydrogen chloride and develops a pressure at room temperature, leakage will be apparent by wetting the paper and giving it an acid reaction. Other mixtures that do not develop pressure can be warmed slightly while in the described position.

the concentrated solution of the sample as it melts and runs down the tube.

In opening tubes that contain an excess of oxidant, especially in the form of chlorine that has been frozen, the rate of thawing must be controlled. If the upper sealed end of the inverted tube warms before the lower end, the vaporization of the chlorine will cause explosive expulsion of the still frozen solution below it. The introduction of a stream of warm distilled water through the lower end and directed at the frozen solution will melt the mass from the bottom to the top. The vaporization of the chlorine will then take place at an even rate with no obstruction to develop pressure.

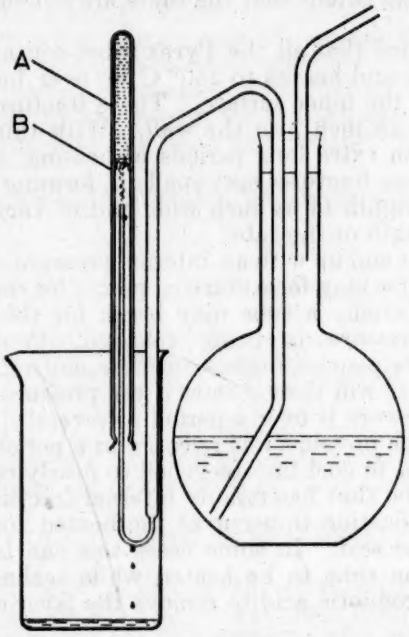

FIGURE 2.—*Method of rinsing solutions from frozen tubes after reaction.*

A, Frozen solution containing liquid chlorine; *B*, warm wash solution.

A wash bottle equipped with a special nozzle of thin-walled tubing of 2-mm bore (2 by 3 mm) in the form of an elongated U is an effective means of melting and washing the reaction tube. The frozen tube is inverted over the U, (fig. 2) and into a tall beaker. As melting takes place, the tube is lowered slowly down the U until the wash liquid cleans all the solution out of the tube.

If there are no volatile end products other than the reactants used to effect the solution, the tube may be opened by heating the end of the tube with a fine flame until a small area gives way and lets the excess internal pressure (or the deficient pressure) blow a small hole through it. Continued heating will cause the glass to flow together and blow out in an orifice, too small to be of use for the removal of solutions, and this phenomenon will repeat itself. Then, while the end of the tube is soft, the flame is held momentarily against the glass below the seal, thereby blowing out a large thin bubble. Heating

the upper portion of this bubble causes it to collapse and fuse into a funnel-shaped cup around the end of the tube with no particles of glass broken off to contaminate the sample. This technic is especially desirable when preparing solutions of materials in which solid residues of silica, titania, etc. are to be determined.

III. REUSE OF THE TUBES

If the emptied tubes are to be used a second time, they should be dried and examined carefully. The inner surfaces are usually damaged [4] by exposure to the acid mixture at high temperature and pressure to such an extent that the tubes are not suitable for repeated use.

It has been noted that all the Pyrex tubes containing hydrochloric acid and chlorine and heated to 250° C or over have shown signs of fine fractures on the inner surface. These fractures penetrate about a thousandth of an inch into the wall. With thin-walled tubing of large diameter, on extra long periods of heating, the glass layer between pairs of these fractures may spall off, forming long thin splinters as much as one-eighth of an inch wide and of varying lengths up to the full inside length of the tube.

With tubes that end up with an interior pressure above atmospheric, these little fractures may form starting points for cracks going through the wall. Occasionally a tube may break for this reason while the compensating pressure is being released. Poulter and Wilson [5] found that liquids penetrate glass surfaces under high pressures and that such a surface will then shatter if the pressure is released, unless the release of pressure is over a period of several days. In the work described here, the pressure was released in a period of about 2 hours (the time required to cool the steel shell to nearly room temperature).

Resealing a tube that has minute internal fractures causes bubbles and some devitrification to occur at the heated zone with great loss of strength of the seal. In some cases this can be prevented if all the surface in the zone to be heated while sealing is treated sufficiently with hydrofluoric acid to remove the layer of glass containing the fractures.

IV. PROTECTION AGAINST EXCESSIVE INTERNAL PRESSURES

In estimating the probable bursting pressures of tubes, the round figure of 10,000 lb/in.^{2} can be used as the tensile strength of glass, if the variability of the strength of glass is kept in mind. The presence of strains and of imperfections in the glass, especially at the surfaces, greatly decreases its strength. If internal and external pressures cannot be balanced, it is better to have the external pressure greater because the outside surface is the more likely to be scratched during the operations prior to heating the tube. An approximate formula for calculating the bursting pressure, A, in lb/in.^{2} of annealed cylindrical glass tubes with well-rounded ends is $A=(2W/D)$ 10,000, in which W is the wall thickness and D is the

[4] For most purposes the contamination of the solution resulting from this damage is negligible. For the amount of glass dissolved, see section IV of RP1621.

[5] T. C. Poulter and R. O. Wilson, Phys. Rev. 40, 877-80 (1932).

internal diameter. Thus, the pressure which a well-made tube of 15-mm bore and 2.5-mm wall thickness may be expected to withstand is over 3,000 lb/in.^{2}. Some of the tubes of this size used in our experimental work have withstood such pressures. Because of the variable strength of glass, however, it is desirable to use a large factor of safety. The recommended conditions as to strength and quantity of hydrochloric acid will not produce pressures in excess of 4,000 lb/in.^{2} at 300° C. It will be seen that, as the diameter of the tubing is decreased, a point is soon reached where external compensating pressure is not needed, especially if an occasional failure, caused by some defect in the glass, can be tolerated. For operations on a micro-analytical scale, C. P. Saylor, of this Bureau, has found the use of capillary tubes (preferably of quartz) of approximately 1-mm bore and wall thickness very satisfactory.

The bursting pressures of samples of the actual tubes to be used and with seals made by the person using them can be conveniently determined by the method described by Gordon.[6] He used the pressures generated by a given specific volume (when completely vaporized) of water to correlate bursting at an observed temperature with the pressure developed inside the tube up to the instant of bursting.

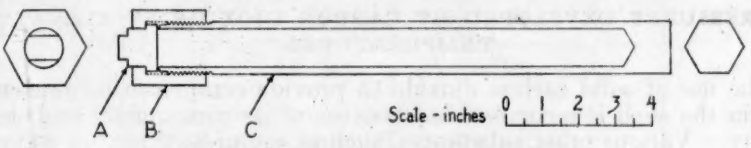

FIGURE 3.—*Steel shell for protection of tube.*

A, Steel head for pressing copper gasket onto knife edge; *B*, graphitic steel nut; *C*, 1⅜-in. hexagonal steel bar, bored out to a diameter of 1 in. threaded for a cap at one end and with a machined knife edge.

V. DESIGN AND USE OF THE STEEL PROTECTING SHELL

The design and dimensions of an easily constructed steel protecting shell are shown in figure 3. The shell is made from a piece of 1⅜-in. hexagonal steel bar, bored out to a diameter of 1 in. and to within a ½ in. of the closed end. The open end is threaded (leaving a uniform ⅛-in. wall thickness uncut) to receive a heavy steel cap, and the rim is carefully machined to a knife edge of about 120°. A disk of soft copper, placed in a recess in the cap, seats against the knife edge and thus provides an effective seal when the cap is screwed on with moderate pressure. The cap is preferably made in two parts, the threaded portion of graphitic steel which will not gall or freeze when screwed on to the ordinary steel, and an ordinary steel insert to bear the copper disk against the knife edge. If the cap is made of the same steel as the shell, the threads are coated with graphite (Aquadag is satisfactory) to keep the threads from freezing.

In the bottom of the shell, which is about 4 inches longer than the tube it is to contain, is put enough calcium carbonate to neutralize all the acid in the tube in the unexpected event of its breaking. The possibility of corrosion of the steel and of dangerously high pressures of hydrogen within the shell are thus avoided. It is desirable to

[6] C. L. Gordon, *Modification of the Carius combustion tube to minimize losses by explosion; Pressures attained on heating nitric acid to 300° C*, J. Research NBS **30**, 107 (1943) RP1521.

wrap the glass tube in a little asbestos yarn to keep it out of contact with the wall of the shell. After the tube is slipped into the shell, solid carbon dioxide is added in an amount calculated to give the desired pressure at the operating temperature. Then the cap is quickly screwed on. After the shell comes to room temperature, it can be tested for tightness by immersing it in water. If the knife-edge is flawless, a few trials will soon indicate how tightly the cap must be screwed on to make a good seal. Seals that do not leak at room temperature are not likely to leak at the higher temperatures, even though the pressure becomes considerably higher.

The shell should be tilted gently a few times to distribute the sample within the tube and then laid horizontally in an oven, which can be kept within a few degrees of the desired temperature.[7] When the heating period is over, the shell is allowed to cool to room temperature before unscrewing the cap to release the carbon dioxide. If inspection shows that the sample has not been completely attacked, the tube can be returned to the shell for further heating.

1. PRESSURES DEVELOPED BY CARBON DIOXIDE AT ELEVATED TEMPERATURES

The use of solid carbon dioxide to provide compensating pressure within the shell is recommended because of its convenience and simplicity. Various other substances, such as compressed air,[8] or water,[9] can of course be used. Although the pressure-temperature curves of carbon dioxide, for various densities, do not match the vapor-pressure curves of hydrochloric acid very closely, they do so more nearly than the pressure temperature curves of air or the vapor-pressure curve of water. In figure 4 are shown ranges of pressures observed in a tube half-full of a mixture of hydrochloric and nitric acids, the vapor pressure curve of water over the same range, and the calculated pressure-temperature lines for two densities of carbon dioxide. The carbon dioxide lines are drawn on the basis of extrapolations by C. S. Cragoe, of this Bureau, of observations by Michels-Veraart.[10] The values are considered to have an accuracy of the order of 1 percent. These data can be interrelated with sufficient accuracy for the present purpose by the equation:

$$\rho=\frac{P-750}{53.8t}+0.060 \qquad (1)$$

for the range $t=250°$ to 300°C, $P=2{,}200$ to 5,900 lb/in^2.

ρ=grams of CO_2 to use per cubic centimeter to produce the desired pressure.
P=protecting pressure desired, pounds per square inch.
t=temperature degree centigrade.

It will be seen that densities of carbon dioxide required to provide a compensating pressure nearly equal to that of the acid mixture at

[7] In the absence of a suitable oven the shell itself can be made into a furnace by wrapping it with a layer of asbestos paper and then with a coil of resistance wire. The proper temperature can be maintained by the use of a thermocouple soldered to the shell near its middle, with suitable additional equipment, as a thermostatting device.

[8] E. Wichers and W. G. Schlecht, *Solution of osmiridium and other refractory materials in acids at high temperatures*, NBS Tech. News Bul. 284, p. 108 (December 1940).

[9] L. A. Greenberg, *Bomb furnace for Carius digestion*, Ind. Eng. Chem., Anal. Ed. **16**, 308 (1944).

[10] C. A. M. Michels-Veraart, *Some physical properties of compressed carbon dioxide*. Thesis, University of Amsterdam, 1937.

the operating temperature involve some excess external pressure at room temperature. This difference need not exceed 1,000 lb/in^2. This is not excessive, except for very large tubes, especially since the glass tubes are usually more resistant to crushing loads than bursting loads. Water is far less desirable as a means of providing the compensating pressures not only because of the nature of its vapor-pressure curve (see fig. 4), but also because of its corrosive effect on glass. No doubt some other substance, or mixture, could be found

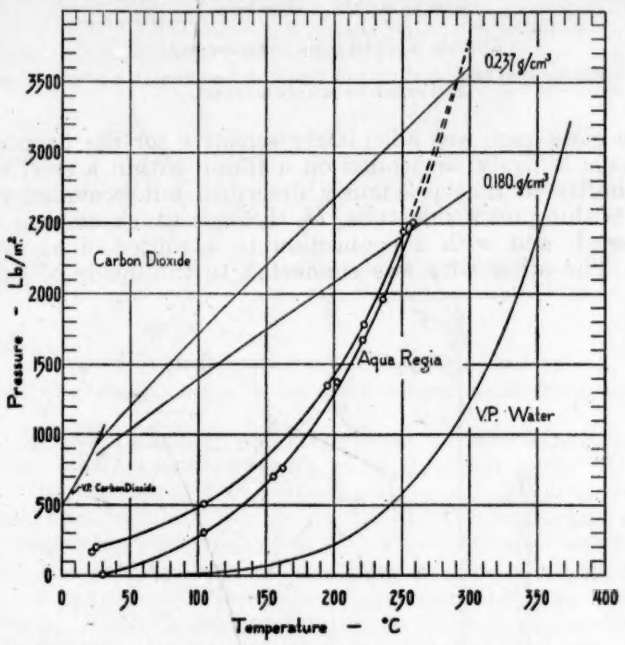

FIGURE 4.—*Pressures developed by 5 ml of aqua regia.*

A mixture of 20 volumes of hydrochloric acid, 36 weight-percent of HCl, and 1 volume of nitric acid, 91 weight-percent HNO_3 at constant volume on heating. Pressures developed by carbon dioxide and water are given for comparison.

to balance the pressure within the sealed tube more closely than carbon dioxide, if it were necessary to do so.

A simple way to test the steel shell for leaks during a period of heating is to weigh it before and after heating.

VI. AN ALL-GLASS (OR QUARTZ) PRESSURE GAGE

To measure the pressures developed by hydrochloric acid and other acids at high temperatures, a gage was constructed. Its design was based on a suggestion made by L. B. Tuckerman, of this Bureau. It is shown in figure 5. It is essentially a moderately long U-tube, made of quartz or Pyrex glass (both were used) with the bend flattened somewhat to increase the sensitivity to changes in pressure, which occur when the temperature of the acid mixture sealed in the gage is changed.

To determine its sensitivity, one of the gages was attached to a mercury manometer. A pressure difference of about 7 cm of Hg (about _ lb/in.^{2}) was required to reclose the contact after the circuit was just broken. The sensitivity of the Bourdon gage used in the measurements of pressure to be reported was between 5 and 10 lb/in.^{2}

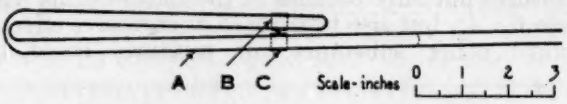

FIGURE 5.—*All glass pressure gage.*

A, Glass U-tube with flattened bend; *B*, clamp with hard Pt-Ir bead for contact point; *C*, clamp with Pt sheet surface for ease of adjustment.

Hence the glass gage was adequately sensitive for the purpose. In use, the gage is freely suspended on a frame within a steel shell, *A* (fig. 6), similar to that previously described but provided with an insulated bushing on a side tube, *D*, through which one wire of the circuit passed, and with a connection to a source of variable gas pressure. The other wire was connected to the inside of the shell.

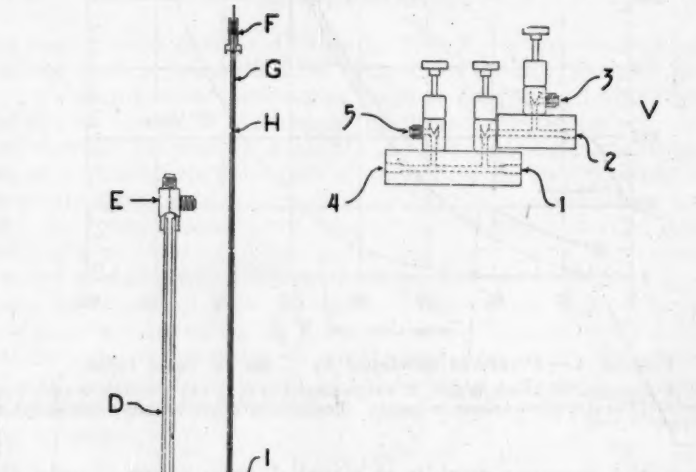

FIGURE 6.—*Apparatus for measuring pressures developed on heating acids.*

A to *K*, Steel shell and insulated connection; *L* to *Q*, glass gage and supporting frame; *V*, valve system.

Outside the oven in which the shell was heated the circuit was completed through a small source of power and a sensitive milliammeter. The meter served only as an off-and-on indicator but usually gave preliminary warning by flickering when the circuit was about to be

broken. The temperature of the system was measured by means of a copper-constantan couple hard-soldered to the outside of the shell (at *T*) and connected to a student-type potentiometer.

During the pressure determinations the gage was suspended as shown in figure 6, *L* to *Q*, on a steel frame, *N*, by fine platinum-wire loops, *O*. The contacts clamped on the arms of the gage had fine platinum wires attached to make the connections to the electric circuits. One wire was protected by an insulating sleeve, *L*, to prevent grounding and a consequent short-circuit. The suspended gage was slid into the steel shell (fig. 6, *A*) with the U horizontal, so that the whole assembly was well back of the side tube.

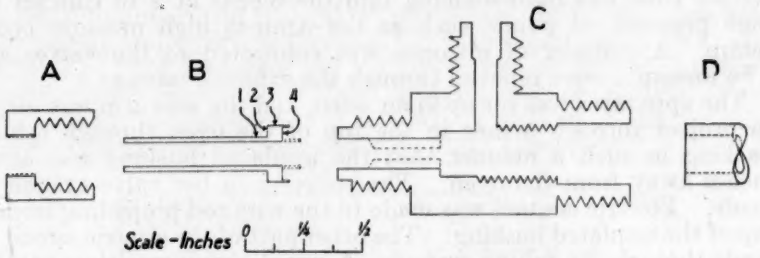

FIGURE 7.—*Construction of insulated bushing.*

A, Threaded collar; *B*, insulated tube; *C*, connection to auxiliary pressure; *D*, connection to steel shell.

The insulated bushing was made from parts of a needle valve and connector as shown in figure 7. The threaded collar of the female part of the connector was reamed out to 11/64-in., as shown at *A*. The steel section of the female part of the connector had the tubular center projection removed, as at *B*. The valve seat was removed by reboring the through-hole of the valve to 1/8 in. This part of the valve was placed over the tube *D* and hard-soldered to it. A fine iron rod of length to just protrude into the autoclave when inserted through the tube *D* was hard-soldered into the steel part, *B*. Porcelain or thin glass insulators were slid over the wire and a fine connecting wire was hard-soldered to the exposed lower end. The bead of solder served to keep the insulators in place.

Insulation was obtained by use of cardboard and a special packing compound made by beating two white facial tissues into a solution of 6 to 7 g of zinc chloride in 100 g of water. The insulation was packed in the following manner: Referring to *B* (fig. 7), a small cardboard collar was placed around the shaft at 1, a small toroid of packing compound (rolled out and slightly blotted) was laid around the shaft at 2, a collar of cardboard was placed around the rim 3, and the threaded cap *A* was carefully pushed onto the shaft. Finally, a toroid of packing compound was laid in the connector seat 4 and around the insulated rod.

When the assembly was screwed into the valve base, the flexible wire attached to the bottom of the insulated iron rod would often coil up, but it could be pulled out straight so that a connection with the insulated wire from the gage could be made outside the autoclave. This connection was wrapped in thin asbestos paper and then tucked

into the free space at the end of the shell. The other wire from the gage was hard-soldered to the center of the copper disk gasket, and was also tucked in the free space. The cap was then screwed tightly onto the copper gasket.

The side arm of the bushing was connected by means of a packed union to ⅛-in. copper tubing connecting through a valve system (shown at *V*, fig. 6) to the auxiliary pressure apparatus (not shown). The valve system was made by boring and threading two brass blocks so as to mount three valves as shown. The copper tube from the autoclave was hard-soldered into the blocks at 1. A copper tube connecting to a Bourdon gage was hard-soldered into the blocks at 4. Another copper tube was hard-soldered into the blocks at 2 to connect to a high pressure oil pump, such as the Aminco high pressure booster pump. A cylinder of nitrogen was connected to the valves at 3. The pressures were relieved through the exhaust valve at 5.

The apparatus was set up in an oven, and the side arm was allowed to project through a hole in the top of the oven through asbestos packing in such a manner that the insulated bushing was several inches away from the oven. The coupling to the valve system was made. Electric contact was made to the wire rod projecting from the top of the insulated bushing. The other part of the electric circuit was made through the tubing system. A signal circuit was thus provided on connecting a battery and millivoltmeter in series with these contacts.

In use, the temperature of the apparatus was raised, and as the signal circuit was broken the pressure in the apparatus was increased by admission of nitrogen from the tank by opening the valve at 3 and then bleeding the gas to the apparatus through the valve at 1. When the pressure required was greater than that delivered by the tank, the gas chamber of the oil pump was allowed to fill, and the valve at 3 was then closed. The valve at 1 was opened, and the pump was operated to raise the pressure to the desired value. Then closing the valve at 1 left only the steel shell and the gage connected. While cooling the apparatus, with consequent lowering of the pressure, the gas in the steel shell was released by opening the valve at 5.

To begin a series of measurements, the glass or quartz gage, which had a capacity of 11.7 ml, was charged with 5 ml of the acid to be studied and sealed without removing the air in the unfilled part. Contacts on the gage were adjusted at room temperature and the gage was placed in the steel shell, which in turn was put in the oven. The temperature of the oven was raised stepwise and held constant at each step until the gage came to a steady balance with the adjusted external pressure. After reaching the highest temperature at which readings were to be made, the temperature was lowered by steps to the starting point. In the measurements on acid mixtures, reactions which occurred changed the composition of the system, hence the temperature-pressure curve did not retrace itself exactly, but closely enough to indicate whether any substantial displacement might have occurred in the gage. Repeated observations at a selected temperature were constant within the sensitivity of the Bourdon gage (5 to 10 lb/in.^{2}).

VII. PRESSURES DEVELOPED BY ACID MIXTURES AT ELEVATED TEMPERATURES

In order to fix at least approximately the compensating pressures that should be provided in the steel protecting shell used in the experimental work on refractory materials, [11] it was necessary to know the pressures developed by hydrochloric acid and its mixtures with suitable oxidizing agents in the temperature range over which the experiments were conducted. Since no such data appeared to be available, measurements were made of nine systems, as follows: Hydrochloric acid of 3 strengths, 23, 36, and 48 weight-percent of HCl; a mixture of 20 volumes of hydrochloric acid (36 weight-percent of HCl) with one volume of fuming nitric acid (91 weight-percent of HNO_3); a mixture of 10 volumes of hydrochloric acid (36 weight-percent of HCl) with 1 volume of perchloric acid (60 weight-percent of $HClO_4$); hydriodic acid (56 weight-percent of HI); and three different amounts of fuming nitric acid (91 weight-percent of HNO_3). The data on fuming nitric acid were given in a previous paper by C. L. Gordon.[12]

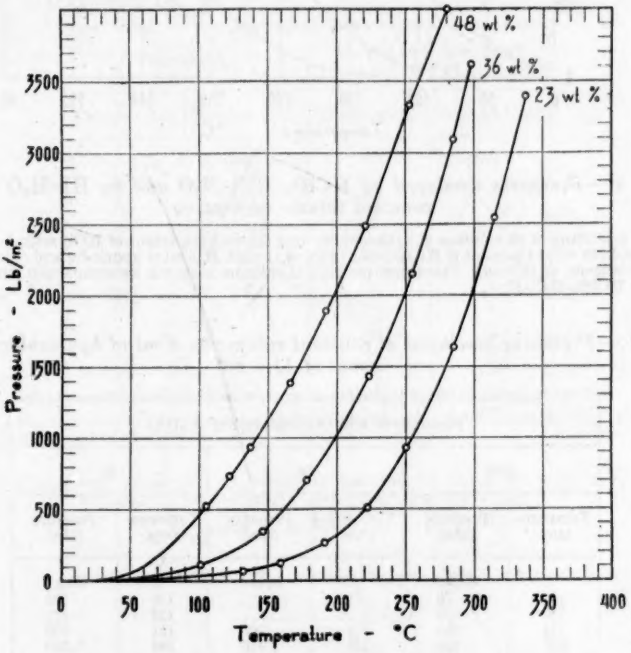

FIGURE 8.—*Pressures developed by hydrogen-chloride solutions of various strengths at constant volume of heating.*

5 ml of acid solution in 11.7-ml space.

The observations on hydrochloric acid are given in table 1 and are shown in figure 8; those on the two mixtures are given in tables 2 and 3 and shown in figures 4 and 9, respectively. The observations on hydriodic acid are given in table 4 and included in figure 9.

[11] See footnotes 1 and 2.
[12] See footnote 5.

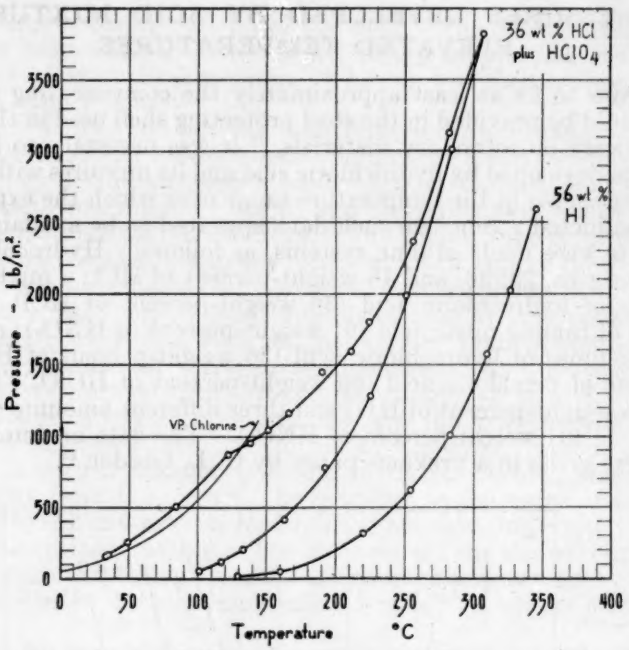

FIGURE 9.—*Pressures developed by* $HClO_4$–HCl–H_2O *and by* HI–H_2O *mixtures at constant volume on heating.*

A, 5 ml of a mixture of 10 volumes of hydrochloric acid (36 weight-percent of HCl) with 1 volume of perchloric acid (60 weight-percent of $HClO_4$) in a space of 11.7 ml; *B*, 5 ml of hydriodic acid (56 weight-percent of HI) in a space of 11.7 ml. The vapor pressure of chlorine is shown for comparison with the product curve for $HClO_4$–HCl–H_2O.

TABLE 1.—*Pressures developed at constant volume by 5 ml of hydrochloric acid in a space of 11.7 ml*

Strength of acid (weight-percent of HCl)					
22.9		36		48	
Temperature	Pressure (abs)	Temperature	Pressure (abs)	Temperature	Pressure (abs)
°C	lb/in.²	°C	lb/in.²	°C	lb/in.²
132	70			105	525
159	125			122	735
191	265	178	705	137	935
220	510	223	1, 430	166	1, 385
250	920	255	2, 150	192	1, 895
285	1, 640	285	3, 095	221	2, 490
315	2, 550	298	3, 615	253	3, 335
338	3, 400			270	3, 995

TABLE 2.—*Pressures developed at constant volume by 5 ml of aqua regia made with 20 volumes of hydrochloric acid (36 weight-percent of* HCl*) plus 1 volume of fuming nitric acid (91 weight-percent of* HNO_3*)*

First heating		Subsequent heatings after heating to about 250° C	
Temperature	Pressure (abs)	Temperature	Pressure (abs)
°C	lb/in.²	°C	lb/in.²
25	10	22	165
106	305	25	200
155	705	104	508
162	765	195	1,350
202	1,375	222	1,780
221	1,670	251	2,440
236	1,960	---	-----
258	[a]2,505	---	-----

[a] Final pressure established after heating at 258° C for a total of about 5 hours.

TABLE 3.—*Pressures developed at constant volume by 5 ml of hydrochloric acid (36 weight-percent of* HCl*) plus 0.5 ml of perchloric acid solution (60 weight-percent of* $HClO_4$*) in a space of 11.7 ml*

First heating		Cooling and subsequent heatings	
Temperature	Pressure (abs)	Temperature	Pressure (abs)
°C	lb/in.²	°C	lb/in.²
101	55	282	3,125
117	120	256	2,365
133	205	224	1,800
163	415	211	1,595
191	780	190	1,450
225	1,285	166	1,165
251	1,985	151	1,045
284	3,010	138	955
307	[a]3,825	122	870
----------	----------	84	505
----------	----------	49	255
----------	----------	35	165
----------	----------	33	155

[a] 3,825 lb/in.² was the equilibrium pressure established after being maintained at 307° for 16 hr. A total rise of 10 lb/in.² was noted during this period.

TABLE 4.—*Pressures developed at constant volume by 5 ml of hydriodic acid (56 weight-percent of* HI*) in a space of 11.7 ml*

Temperature	Pressure (abs)
°C	lb/in.²
129	20
160	50
190	165
220	320
254	620
283	1,010
310	1,570
327	2,020
346	2,490

If the data for the hydrochloric acid determinations, table 1, are plotted in the form of $\log_{10}$ of the pressure (abs) as a function of reciprocal absolute temperature, it can be noted that the three lines through the points representing temperatures from 200° to 300° C (see fig. 10) nearly intersect in a point. For the purpose of

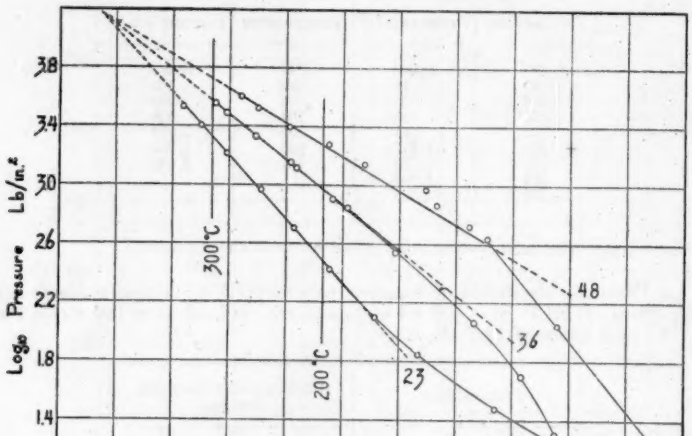

FIGURE 10.—*Logarithm of pressure as a function of temperature for three strengths of hydrochloric acid.*

predicting the pressure of an acid of any composition within the range 23 to 48 percent by weight, at temperatures between 200° and 300° C, these lines were forced to coincide at one point, and an equation of the pressure as a function of the temperature and of the composition was derived. The equation for the range 23 weight-percent to 48 weight-percent and 200° C to 300° C, is

$$\text{Log}_{10}\, P=\left(\frac{1000}{T}-1.345\right)\left[\tan\,(0.615W+100.7)\right]+4.180,$$

where P is the pressure in lb/in.² attained at $T°K$ by a solution of W weight-percent of HCl in a tube which is 43 percent filled by the acid at room temperature. The angle, of which the tangent is to be used in the equation, is here expressed as degrees.

WASHINGTON, May 25, 1944.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1623

Part of Journal of Research of the National Bureau of Standards, Volume 33, December 1944

ANALOGY OF HYDRATED CALCIUM SILICOALUMINATES AND HEXACALCIUM ALUMINATE TO HYDRATED CALCIUM SULFOALUMINATES

By E. P. Flint and Lansing S. Wells

ABSTRACT

Two hydrated calcium silicoaluminates were prepared, which appear to be the silica analogs of the hydrated calcium sulfoaluminates. The low-silica compound has the formula, $3CaO.Al_2O_3.CaSiO_3.12H_2O$. It occurs as hexagonal plates, is uniaxial negative, and has the indices of refraction, $\omega=1.538$, $\epsilon=1.523$. The other compound occurs as needle-shaped prisms and is uniaxial negative; $\omega=1.487$, $\epsilon=1.479$. It was not obtained in pure form but, by analogy with other calcium aluminate complex salts, was tentatively assigned the formula, $3CaO.Al_2O_3.3CaSiO_3.30$–$32H_2O$. The low-silica compound is slowly converted to the high-silica silicoaluminate on standing in contact with lime solutions. The high-silica compound was identified in mixtures of β-$2CaO.SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$; β-$2CaO.SiO_2$ and $3CaO.Al_2O_3$; and $3CaO.SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$ which had stood in contact with approximately saturated lime solution for 3 years. A hydrated hexacalcium aluminate, $6CaO.Al_2O_3.33H_2O$, was prepared. It occurs as long, needle-like prisms, is uniaxial negative, and $\omega=1.475$, $\epsilon=1.466$. Its formula may be written as $3CaO.Al_2O_3.3Ca(OH)_2.30H_2O$, which indicates that it is the compound formed when the $CaSO_4$ in the high-sulfate sulfoaluminate is completely replaced by $Ca(OH)_2$.

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I. INTRODUCTION

The high-sulfate form of calcium sulfoaluminate, $3CaO.Al_2O_3.3CaSO_4.31H_2O$, is a constituent of hydrated portland cement and is also produced by the action of sulfate waters on concrete [1].[1] Another compound, $3CaO.Al_2O_3.CaSO_4.12H_2O$, discovered by Lerch, Ashton, and Bogue [2], and known as the low-sulfate form of calcium sulfoaluminate, has not been identified in hydrated portland cement. Numerous other calcium aluminate complex salts have been synthesized in which the $SO_4^=$ radical of both the high- and low-sulfate forms is completely replaced by various acid radicals. A list of the compounds that have been prepared is given in table 1.

[1] Figures in brackets indicate literature references at the end of this paper.

TABLE 1.—*Calcium aluminate complex salts that have been synthesized by various investigators* [3]

Type I [1]	Type II [2]
$3CaO.Al_2O_3.3CaSO_4.31H_2O$	$3CaO.Al_2O_3.CaSO_4.12H_2O$
$3CaO.Al_2O_3.3CaCO_3.27H_2O$	$3CaO.Al_2O_3.CaCO_3.11H_2O$
$3CaO.Al_2O_3.3Ca(ClO_3)_2.30H_2O$	$3CaO.Al_2O_3.Ca(ClO_3)_2.10H_2O$
$3CaO.Al_2O_3.3Ca(CH_3CO_2)_2.30H_2O$	$3CaO.Al_2O_3.Ca(CH_3CO_2)_2.8H_2O$
$3CaO.Al_2O_3.3CaCrO_4.30H_2O$	----------
$3CaO.Al_2O_3.3CaSeO_4.30H_2O$	----------
$3CaO.Al_2O_3.3CaMnO_4.30H_2O$	----------
$3CaO.Al_2O_3.3Ca(IO_3)_2.30H_2O$	----------
$3CaO.Al_2O_3.3Ca(HCO_3)_2.30H_2O$	----------
$3CaO.Al_2O_3.3Ca(C_2H_3CO_2)_2.30H_2O$	----------
----------	$3CaO.Al_2O_3.CaCl_2.10H_2O$
----------	$3CaO.Al_2O_3.CaBr_2.10H_2O$
----------	$3CaO.Al_2O_3.CaI_2.8H_2O$
----------	$3CaO.Al_2O_3.Ca(NO_3)_2.10H_2O$
----------	$3CaO.Al_2O_3.Ca(NO_2)_2.10H_2O$

[1] General formula: $3CaO.Al_2O_3.3CaX.30\text{-}32H_2O$ or $3CaO.Al_2O_3.3CaY_2.30\text{-}32H_2O$, where X is a bivalent and Y a univalent acid radical.

[2] General formula: $3CaO.Al_2O_3.CaX.8\text{-}12H_2O$ or $3CaO.Al_2O_3.CaY_2.8\text{-}12H_2O$, where X is a bivalent, and Y a univalent acid radical.

In spite of the fact that silica is the most abundant acidic oxide in portland cement, no previous attempts have been made to prepare the analogs of the calcium sulfoaluminates which would contain the silicic acid radical, $SiO_3^=$. The present paper is a preliminary report on attempts to synthesize such compounds and also to obtain a replacement of $CaSO_4$ in the high-sulfate calcium sulfoaluminate by $Ca(OH)_2$. The data are presented at this time because it is anticipated that the completion of a more extensive study of these compounds may be somewhat delayed.

II. EXPERIMENTAL PROCEDURE AND RESULTS

1. PREPARATION OF HYDRATED CALCIUM SILICOALUMINATES

The silicoaluminate precipitates were made by a modification of a method that has been commonly used in preparing other complex salts of the calcium aluminates. This method consisted in mixing solutions of calcium silicate and aluminate in the desired proportions and in adding various amounts of solid calcium oxide.

A 20-liter volume of calcium silicate solution was prepared, according to a method described previously [4], by boiling purified silica gel with dilute calcium hydroxide solution (0.1 g of CaO per liter) for about 18 hours and removing the undissolved residue by filtration. The filtrate contained 0.0303 g of CaO and 0.387 g of SiO_2 per liter. A quantity of calcium aluminate extract was obtained by shaking 200 g of low-sulfate calcium aluminate cement (0.03 per cent of SO_3) with 4 liters of distilled water for 3 hours, filtering, and diluting the extract to 12 liters. The resulting solution contained 0.400 g of CaO and 0.581 g of Al_2O_3 per liter.[2]

[2] It has been shown [9] that calcium aluminate solutions prepared from commercial calcium aluminate cements are practically free of iron. More recent studies have revealed that the quantity of silica extracted is so small that for the purpose at hand it may be neglected. The concentration of alkalies in the solution should have been too low to be a factor of moment because: first, a low-alkali cement was used in their preparation; second, a very high water-cement ratio was maintained; and, third, the solutions were subsequently diluted.

As shown in table 2, mixtures of the calcium aluminate and silicate solutions were prepared in which the molar ratios of silica to alumina varied between 1 and 4. Quantities of solid calcium oxide were then immediately added to the mixtures in amounts sufficient to saturate the solutions with calcium hydroxide (1.15 g of CaO per liter) and in addition to provide molar ratios of total lime to alumina ($CaO/Al_2O_3 + CaSiO_3/Al_2O_3$) varying between three and seven in the precipitates. The precipitate in experiment 1, table 2, had the typical "silken" appearance of suspensions of the hexagonal hydrated calcium aluminates. This characteristic was exhibited in diminishing degree by the precipitates in experiments 2, 3, and 4 and not at all by those in experiments 5 and 6. The mixtures, in well-stoppered flasks, were shaken for 15 minutes to disperse the added lime and thereafter at hourly intervals during the first day. The flasks were stored in the laboratory and subsequently shaken once daily in the course of the first month, after which they were allowed to stand without shaking. Samples of the precipitates were withdrawn at intervals for microscopical examination.

TABLE 2.—*Preparation of hydrated calcium silicoaluminates*

Experiment number	Composition of mixture			Elapsed time before analysis of samples of precipitate and solution	Molar ratios in precipitate					CaO content of solution
					Calculated		By analysis			
	Calcium aluminate solution [1]	Calcium silicate solution [2]	Solid CaO		$\frac{CaO}{Al_2O_3}$	$\frac{CaSiO_3}{Al_2O_3}$	$\frac{CaO}{Al_2O_3}$	$\frac{CaSiO_3}{Al_2O_3}$	$\frac{H_2O}{Al_2O_3}$ [3]	
	ml	*ml*	*g*	*Days*						*g/liter*
1	2,000	1,769	6.04	27	3	1	2.95	1.05	12.3	1.14
2	1,000	1,769	3.69	60	1	2	2.00	2.09	12.3	0.53
3	1,000	1,769	4.33	59	3	2	3.00	2.05	13.5	1.11
4	1,000	1,769	4.65	60	4	2	3.70	2.15	14.8	1.24
5	1,000	2,654	5.64		3	3				
6	500	1,769	3.47	198	3	4	3.38	4.27	19.2	1.09

[1] Contained 0.581 g of Al_2O_3, 0.400 g of CaO per liter.
[2] Contained 0.387 g of SiO_2, 0.0303 g of CaO per liter.
[3] Determined after washing precipitate with alcohol and ether, and drying to constant weight in a desiccator over calcium chloride.

The precipitate from experiment 1 became uniform in index of refraction within about 1 week. Although very finely divided, it appeared to be entirely composed of very small hexagonal plates, frequently occurring in spherulitic groups. The crystals are uniaxial negative and have the refractive indices, $\omega = 1.538 \pm 0.003$, $\epsilon = 1.523 \pm 0.003$. Chemical analyses of the precipitate, after it had stood in contact with solution for 27 days, gave the molar ratios shown in table 2, which correspond to the formula $3CaO.Al_2O_3.CaSiO_3.12H_2O$. The X-ray diffraction pattern of the preparation is similar to those of $3CaO.Al_2O_3.CaSO_4.12H_2O$ and of $4CaO.Al_2O_3.13H_2O$ (or $3CaO.Al_2O_3.Ca(OH)_2.12H_2O$), with a closer relationship to $4CaO.Al_2O_3.13H_2O$.

In experiment 2, table 2, the preparation which contained CaO, Al_2O_3, and $CaSiO_3$ in the molar ratios 1:1:2 took up lime from solution and gave molar ratios of 2:1:2 in the precipitate. The molar ratios of the other analyzed precipitates agreed approximately with the calculated values. All of the preparations listed in table 2, except that

of experiment 1, contained considerable finely divided or amorphous material as well as hexagonal plate crystals having the optical properties of $3CaO.Al_2O_3.CaSiO_3.12H_2O$. Their X-ray diffraction patterns corresponded with that of this compound. It was concluded, therefore, that the only silicoaluminate formed in these mixtures is the compound $3CaO.Al_2O_3.CaSiO_3.12H_2O$.

After these determinations, the mixtures were allowed to stand for an additional 3 years and samples of the precipitates were again withdrawn for microscopical examinations. A new phase was then observed in the precipitates. It appeared usually as long, thin needlelike prisms. In some preparations where the crystals had a greater width, the prisms appeared to possess a hexagonal cross-section. They are uniaxial negative, $\omega=1.487\pm0.003$, $\epsilon=1.479\pm0.003$. The crystals have parallel extinction and negative elongation.

Table 3 shows the approximate proportions of these crystals in the various precipitates. In each precipitate the more abundant phase consisted of the hexagonal plate form of silicoaluminate. No isometric crystals were found, thus indicating the absence of members of the garnet-hydrogarnet series [10].

TABLE 3.—*Formation of needle crystals of calcium silicoaluminate in preparations of table 2, after standing for 3 years in contact with lime solutions*

Experiment number	Approximate molar ratios in precipitate		Approximate proportion of needle crystals in precipitate	CaO in solution
	$\frac{CaO}{Al_2O_3}$	$\frac{CaSiO_3}{Al_2O_3}$		
			%	*g/liter*
1	3	1	20	0.530
2	1	2	30	.344
3	3	2	40	.832
4	4	2	40	.905
5	3	3	40	.663
6	3	4	5	.541

The needle crystals are believed to be a high-silica calcium silicoaluminate, $3CaO.Al_2O_3.3CaSiO_3.XH_2O$. The habit of these crystals and the measured optical properties, except indices of refraction, are identical with those of the high-sulfate calcium sulfoaluminate, $3CaO.Al_2O_3.3CaSO_4.31H_2O$. A water content of 30 to 32 moles is tentatively assigned to the silicate compound by analogy with the various similar calcium aluminate complex salts which have been prepared.

The behavior of the low-silica form of calcium silicoaluminate in converting slowly to the high-silica form is entirely similar to the relations exhibited by the calcium sulfoaluminates. Thus, in the preparation of the high-sulfate calcium sulfoaluminate, Lerch, Ashton, and Bogue [2] observed that the low-sulfate compound was usually obtained as an intermediate product, despite the presence of an excess of $CaSO_4$. The conversion to the more stable sulfoaluminate is usually complete in about a week, whereas the corresponding transformation, in the case of the silicoaluminate compounds, is incomplete after 3 years, even in experiment 5, where CaO, Al_2O_3, and SiO_2 were in the proper proportions to form the high-silica product.

The precipitates in experiments 4 and 5 of table 3 gave the X-ray diffraction pattern of $3CaO.Al_2O_3.CaSiO_3.12H_2O$, together with additional lines. Because of the obscuring effect of the stronger pattern it was not possible to determine whether these additional lines indicated an X-ray diffraction pattern similar to that of the high-sulfate calcium sulfoaluminate.

The lime contents of the solutions after 3 years' contact with the silicoaluminate precipitates are shown in the last column of table 3. These values indicate that the high-silica calcium silicoaluminate will form in the presence of solutions containing between 0.3 and 0.9 g of CaO per liter.

2. FORMATION OF HIGH-SILICA CALCIUM SILICOALUMINATE FROM MIXTURES OF CEMENT COMPOUNDS

In order to determine if hydrated calcium silicoaluminate will form from mixtures of the various cement compounds in saturated lime solution, the combinations of anhydrous calcium aluminates and silicates shown in table 4 were prepared. The mixtures, which contained the compounds in equimolar proportions, were added to 1-liter portions of saturated lime solution (1.15 g of CaO per liter) and placed in tightly stoppered flasks, which were allowed to stand for 3 years with occasional shaking. Samples were then withdrawn for microscopical examination.

TABLE 4.—*Formation of needle crystals of calcium silicoaluminate in mixtures of cement compounds placed in saturated lime solution (1.15 g CaO per liter) and allowed to stand for 3 years*

Experiment number	Mixture [1]	Weight of mixture per volume of lime solution	Approximate proportion of needle form of silicoaluminate in product	CaO in solution
		g/liter	*%*	*g/liter*
1	β-$2CaO.SiO_2$+$4CaO.Al_2O_3.Fe_2O_3$	18	10	1.02
2	β-$2CaO.SiO_2$+$3CaO.Al_2O_3$	10	30	1.11
3	$3CaO.SiO_2$+$4CaO.Al_2O_3.Fe_2O_3$	10	15	1.08
4	$3CaO.SiO_2$+$3CaO.Al_2O_3$	10	0	1.15

[1] The mixtures contained equimolar proportions of the compounds.

As shown in table 4, all of the products, except that from the mixture of tricalcium aluminate and tricalcium silicate, contained appreciable amounts of the high-silica calcium silicoaluminate, which appeared as well-developed needle-like prisms. Hexagonal plate crystals were also present in the materials. No attempt was made to identify the crystalline phases which made up the balance of the products.

The lime contents of the solutions given in the last column of table 4, in conjunction with similar data in table 3, indicate that the high-silica silicoaluminate can form in contact with solutions containing calcium hydroxide in amounts between 0.3 g of CaO per liter and saturation.

3. PREPARATION OF HYDRATED HEXACALCIUM ALUMINATE

Assarsson [5] observed the precipitation of needle-shaped hexagonal prisms from extracts of monocalcium aluminate and high-alumina cements. He assigned to this material the formula $5CaO.Al_2O_3.34H_2O$,

but stated, in his discussion of a paper by Bessey [6], that it seems to be impossible to prepare the compound without any trace of sulfate. Wells, Clarke, and McMurdie [7] failed to find such an aluminate in the system $CaO–Al_2O_3–H_2O$ at 21° and 90° C, and suggested that it may exist in the quaternary system $CaO–Al_2O_3–CaSO_4–H_2O$ as a metastable phase. Bessey [6] expressed the opinion that the compound may be related in structure to the high-sulfate form of calcium sulfoaluminate.

The preparation of such an aluminate was attempted in order to determine if the calcium sulfate in $3CaO.Al_2O_3.3CaSO_4.31H_2O$ can be completely replaced by calcium hydroxide. It was anticipated that the highly basic compound which might result from such replacement would only be stable in contact with solutions containing high concentrations of calcium hydroxide.

Accordingly, an excess of calcium oxide was added to 500 ml of a 10-percent sugar solution, the mixture shaken for 3 hours, and filtered. The filtrate contained 17 g of CaO per liter. A calcium aluminate extract was prepared by shaking 50 g of calcium aluminate cement (containing 0.03 percent of SO_3) with 500 ml of water for 3 hours and filtering. This extract contained 1.8 g of Al_2O_3 and 1.2 g of CaO per liter. The solutions were mixed and allowed to stand. Formation of a precipitate began within a few hours. After 5 days, samples of the precipitate and solution were withdrawn. Titration of the solution with standard acid showed a lime content of 9.06 g of CaO per liter. The sample of precipitate was placed in a flask with 100 ml of absolute alcohol and the mixture shaken for 1 hour to remove any sugar from mother liquor adhering to the particles. The solid material was then filtered off, washed with alcohol and ether, and dried in air overnight.

Microscopical examination showed that the preparation consisted of needle-like prisms entirely similar in appearance to crystals of the high-sulfate form of calcium sulfoaluminate. The crystals are uniaxial negative; $\omega=1.475\pm0.003$ and $\epsilon=1.466\pm0.003$. They have parallel extinction and negative elongation.

Analysis of the preparation gave the following composition:

	%
CaO	32.38
Al_2O_3	9.84
H_2O	57.46
Total	99.68

This corresponds to molar ratios of $5.98CaO:1Al_2O_3:33H_2O$. Accordingly, the compound may be assigned the formula, $6CaO.Al_2O_3.33H_2O$ or $3CaO.Al_2O_3.3Ca(OH)_2.30H_2O$. Its X-ray diffraction pattern is almost indistinguishable from that of $3CaO.Al_2O_3.3CaSO_4.31H_2O$.

It is believed that this compound and Assarsson's pentacalcium aluminate hydrate are fundamentally the same and that the lower CaO/Al_2O_3 ratio of Assarsson's compound is caused by partial hydrolysis.

Although qualitative tests of the $3CaO.Al_2O_3.3Ca(OH)_2.30H_2O$ indicated the absence of sulfate, it seemed desirable to prepare it from starting materials in which this constituent was entirely absent.

Accordingly, a calcium aluminate extract was made from sulfate-free $3CaO.5Al_2O_3$ and added to a lime-sugar solution prepared as before. The resulting crystalline precipitate was identical in all respects with that which resulted from mixing the extract of calcium aluminate cement with lime-sugar solution.

III. SUMMARY

Two calcium silicoaluminates, apparently analogs of the high- and low-sulfate forms of calcium sulfoaluminate, were investigated. The low-silica silicoaluminate has the formula, $3CaO.Al_2O_3.CaSiO_3.12H_2O$, and occurs as thin hexagonal plates. In contact with lime solutions, it is slowly converted to long needle-like prisms whose habit and optical properties are very similar to those of $3CaO.Al_2O_3.3CaSO_4.31H_2O$. The needle-form of the silicoaluminate has not yet been prepared in a pure state but, by analogy with other similar calcium aluminate complex salts, it has tentatively been assigned the formula, $3CaO.Al_2O_3.3CaSiO_3.30\text{-}32H_2O$. It was also found in the following mixtures of cement compounds, which had stood in contact with approximately saturated lime solutions for 3 years: β-$2CaO.SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$; β-$2CaO.SiO_2$ and $3CaO.Al_2O_3$; and $3CaO.SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$. The role of the silicoaluminates in the setting and hardening of cements warrants further study. The close analogy between the silico- and sulfoaluminates suggests the possible existence of a solid-solution series between these compounds with the formation of sulfo-silicoaluminates, somewhat similar to those reported by Lafuma [8].

A hexacalcium aluminate hydrate was prepared that appears to be the analog of the high-sulfate form of calcium sulfoaluminate in which calcium sulfate is completely replaced by calcium hydroxide. Its formula may be written as $3CaO.Al_2O_3.3Ca(OH)_2.30H_2O$. This compound would probably not form as a direct hydration product of portland cement but might appear, under some conditions, as a solid solution in the high-sulfate form of calcium sulfoaluminate.

The authors are indebted to H. F. McMurdie for making the X-ray diffraction patterns of the preparations.

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WASHINGTON, September 19, 1944.

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